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On Transient Hot-Wire Determination of the Thermal Conductivity of Pure, Dielectric Liquids

by

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Abstract

A survey is given of the theory of transient hot-wire measurement of the thermal conductivity λ of pure, dielectric liquids. On the basis of the survey two possible sources of error are investigated: convection, which so far has not been studied in every detail; and a thermo-elastic error which appears in certain designs of the measuring cell, and which has not previously been mentioned in the literature.

One of the purposes of the report is to serve as a foundation to which will be referred in a later report, which will deal with a modification of the method worked out by the author for measurement of λ for electrolytic solutions. It has therefore been necessary to deal rather exhaustively with some more trivial and well-known facts regarding the electric circuit analysis and the calculation method for λ in sections V and VI. But the calculation method differs somewhat from the usual one because the modification mentioned made it necessary to use a hot wire of a relatively large diameter (500 μm). In the "classical" versions of the method, as thin a wire as possible is used (20 - 50 μm).

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Contents

I. Purpose and Contents of the Investigation

During the last decades the transient hot-wire method has been increasingly used as a method for measurement of the thermal conductivity of liquids. Briefly, its principle is as follows. The liquid is filled into a cylindric cell vertically placed in a thermostat. Along the axis of the cell a hot wire is located. When an electric current is fed into a circuit of which the cell is a component, heat will flow from the wire into the liquid. The better the liquid conducts the heat away from the wire, the more slowly the wire temperature increases. In addition to its function as a source of heat, the wire therefore acts, in most designs, as a resistance thermometer, which makes it possible to register its temperature versus time curve by means of a recorder built into the circuit. The wire temperature can also be measured by means of a thermocouple. From the curve registered, and from certain other measurements in the system, the thermal conductivity of the liquid can be deduced according to the theory of the method.

The original, "classical" version of the method does not lend itself to measurements on electrolytically conductive liquids. One or more later reports will, however, deal with an investigation concerning a modification of the method to apply to electrolytic solutions. That investigation was carried out at the Danish Atomic Energy Commission Research Establishment Risø, and was completed about 2 years ago. To some extent its basic idea is irrelevant to the present report, but the demonstration that this idea can be carried through without indeterminable sources of error requires a rather accurate analysis. This analysis rests, in its turn, upon the theory of, and the experimental technique used for, the application of the method to dielectric liquids.

The present report deals with the last-mentioned subjects and forms the basis of the work concerning electrolytic solutions.

The report may therefore be viewed from two angles, viz.

1) as a self-contained contribution to the theory of the transient hot-wire method applied to measurements on dielectric liquids, and
2) as a paper to which reference can be made in a later report concerning measurements on electrolytic solutions.

Primarily two possible sources of error - so far overlooked or, perhaps, less thoroughly investigated - are dealt with here. They originate

from:

a) the problem of convection, and

b) certain thermo-elastic aspects of the measuring cells.

a) When the thermal conductivity is to be measured, no convective contributions to the heat flow must occur, unless such contributions can be corrected for, as for example by using another method operating with controlled, forced convection. However, the convection which may appear in hot-wire cells is "free". As the liquid is at rest in the initial state and as a certain time will elapse before the liquid has accelerated to an appreciable velocity field, it is obvious that the convection need not be taken into consideration if the measurement can be completed very quickly. Modern electronic equipment makes such sufficiently quick measurements possible. From the moment the current has been switched on until the first registration can be made, only a few milliseconds may be needed.

However, there are two reasons why the convection problem is discussed rather thoroughly here.

One reason is that only in recent years has it been possible to perform registrations so quickly that one dare ignore, almost by intuition, the convection. The vast majority of published measurements performed by means of the method are therefore made with registrations lasting from ten to fifteen seconds. Nevertheless, most, if not all*, authors claim that no convection occurs during the experiments. This report shows that this is not so. A closer investigation of the convection may therefore be of interest because clear grounds are missing for the assumption that convection did not disturb many of those measurements performed according to the method which yielded some of the values stated in the literature on the thermal conductivity of liquids.

The other reason for the rather exhaustive treatment of convection is the following: The electrolytic solution measurements (which will be reported later) differ somewhat from dielectric liquid measurements as to how soon, after switching on the current, registrations can be made.

To demonstrate this, the idea underlying the modification of the method for measurement on electrolytes must be briefly outlined, although, in principle, the idea has no bearing on this report. In the literature of measurements known by the author, the method has been modified to apply to

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* The present author does not know any exceptions.

such measurements by surrounding the wire by an electrically insulating coat. That this coating is a necessity is often stated explicitly in the literature. Many disadvantages attach, however, to such a coat. Alas (1967) [1] used, for practical and theoretical reasons, a thin coat, which is soluble in bases, on which Alas, therefore, could not perform measurements. He confines himself to solutions of salts. van der Held et al. (1949) [12] employed a glass capillary tube, but his work was revoked in 1953 [13].

However, the present author succeeded in performing measurements with electrically uninsulated wire on bases as well as on acids and salts by arranging the experiment in such a way that a balance was quickly established between the counter-electromotive force from the polarization and the voltage applied to the cell. The liquid behaves then, i.e. for the remainder of the measurement period, as a dielectric. However, the balance is only established after a short current pulse has passed through the liquid, and during the time that elapses before the current pulse fades away, registrations are disturbed. There can therefore a priori be said to be a limit as to how soon measurements on electrolytic solutions can be commenced after the current has been switched on. As far as so-called ideally polarized electrodes are concerned, where chemical processes do not at all participate during the current pulse (a "non-faradayan current pulse"), the author has by theoretical calculations rendered probable that the pulse, in the present context, can be considered practically fading out instantaneously. However, quite ideal polarization cannot always be expected, although the set-up is such that operations are performed below the decomposition voltage of the electrolyte.

The problem of convection may therefore prove to be of more fundamental interest for the measurements on electrolytes than it is nowadays for measurements on dielectric liquids, if sufficiently up-to-date electronic equipment is available. It is therefore desirable to understand the "mechanism" of convection in the apparatus with a view to later investigations.

b) Gillam et al. [4] use a cell as sketched out in fig. 1. The cell is made of glass and the hot wire is of platinum. P,P indicates potential leads, which will be dealt with later. The hot wire is sealed, in a stretched-out state, direct in the glass. This type of cell is extremely simple and robust. Other authors insert a helical spring which keeps the wire stretched out. As far as the present author can see, the helical spring insertion is mainly thought to be used in set-ups in which measurements are made at

various temperatures.

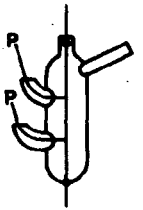

Fig. 1

If the temperature of measurement in a springless device is raised, various risks will, for thermo-elastic causes, be incurred. Since the work of the present author was in the main limited to room temperature, such risks are of minor importance here although a springless cell is used. In the following, however, it is demonstrated that under unfavourable conditions a source of error of thermo-elastic origin may occur in springless devices, also in connection with measurements at a given temperature, as e.g. room temperature. This source of error has so far not been dealt with in the literature on the subject. It too can be eliminated by inserting a properly constructed spring (i.e. a spring of suitable stiffness). However, as is the case with the previous source of error a), also the one mentioned here, the thermo-elastic one, is of interest in connection with the judgement of errors in the data given in the literature. Besides Gillam et al., several other authors, including Alas [1], perform their measurements without helical springs. However, in Alas' measurements, thermo-elastic errors are actually eliminated, a fact which Alas does not explicitly mention, for, as said, these errors are not mentioned in the literature. Alas measures relative to water, and it is shown in this report that by so doing the error is totally eliminated. Relative measurements is therefore, as far as the elimination of the said thermo-elastic error is concerned, an alternative to the method of inserting a spring. Incidentally, if the two liquids whose thermal conductivity ratio is measured resemble each other mechanically and thermally, relative measurements have also other advantages, which will be dealt with later.

Besides an examination of the sources of error mentioned here, the report describes the electric circuit and the calculation method used for the experiments which will be treated in the next report. This subject is of a more elementary nature; it is presented in the sections V and VI, which may be said to contain only little of original character. However, they are included in this report for the sake of future reference, and because they show how the calculation may be performed, and how to build

a circuit, when a hot wire of a considerably larger diameter than those mentioned in the literature is used. In the "classical" versions of the method, it is deemed necessary to attempt to approximate a straight line distribution for the heat production in the cell. The theory is simplified considerably if such an ideal distribution is presupposed. The vast majority of wire diameters mentioned in the literature are 20 - 50 μm. The present investigation departs from this "principle of thin wires", diameters of 500 μm being used. This is due to the transition to measurements on electrolytic solutions to be described in a later report. Although the use of a "thick" wire is due to this transition, the present report ignores all complications arising from the liquid being electrically conductive. It should of course also be possible to use the modified apparatus for measurements on dielectric liquids. In this report such liquids are imagined filled into the apparatus. The cell of the modified apparatus is very robust and simple, and the apparatus may therefore prove useful also for measurements on dielectric liquids.

Section VII contains some short comments on the measurement accuracy of determinations of the thermal conductivity, on other methods than the transient hot-wire determination and on comparisons between the methods.

II. General Macroscopical Aspects of Thermal Conduction in Pure, Dielectric Liquids

"The heat flow equation" plays a fundamental role for the transient measurement of thermal conductivity, and it is derived in this section. In the nature of the case, the section does not contain anything original, but the conditions for applying said equation to pure, dielectric liquids is examined in more detail than is ordinarily the case in the literature on measurements. In the literature, the heat flow equation usually forms the basis (assumed beforehand) of any treatment of transient methods.

In the following the energy transport in the liquid by electromagnetic radiation, i. e. by "thermal radiation", is neglected. To include this transport possibility in the calculations requires rather advanced mathematics and complicated investigations (cf. a study by Leidenfrost [7] on a steady state method for measurement of thermal conductivity). It can be ascertained that, apart from a few exceptions, there is agreement that in the present context it does not pay to initiate such a treatment since simple reasoning

will indicate that radiation can be neglected.

For the treatment of the present problem, the general balance equations of physics ("equations of continuity") for mass, energy and momentum must primarily be applied.

If $\vec{v}$ is the velocity field in the liquid, which - as said in the heading - is supposed to be pure and dielectric; and if we consider a closed surface, O, the points of which move with this velocity (i.e. a closed surface moving with the flow); and if

t = time

$\frac{d}{dt} = \frac{\partial}{\partial t} + \vec{v} \cdot \text{grad}$ (= convective derivative) when operating on a field

ω = the volume enclosed by O

ρ = mass density

u = internal energy per unit mass

$-\mathfrak{P}$ = the sum of the viscosity stress tensor and the hydrostatic pressure tensor

$\vec{j}_u$ = flow density of non-mechanical energy transport

$\vec{n}$ = outward unit normal to O

$\vec{F}$ = external force per unit mass

the energy equation is

$$\frac{d}{dt} \int_\omega \rho \left\{ \frac{\vec{v}^2}{2} + u \right\} d\omega = -\int_O \left\{ \mathfrak{P} \cdot \vec{v} + \vec{j}_u \right\} \cdot \vec{n} \, do + \int_\omega \rho \vec{F} \cdot \vec{v} \, d\omega . \qquad (1)$$

The fields occurring in (1) are functions of cartesian coordinates x, y, z in a coordinate system at rest as well as of time t. Moreover, they are thought to fulfil appropriate conditions of continuity and differentiability. From (1) then follows, by means of Gauss's divergence theorem, and a well-known kinematic theorem that the equation

$$\frac{\partial}{\partial t} \left(\rho \frac{\vec{v}^2}{2} + \rho u \right) + \text{div} \left\{ \left(\rho \frac{\vec{v}^2}{2} + \rho u \right) \vec{v} \right\} = -\text{div} \mathfrak{P} \cdot \vec{v} + \rho \vec{F} \cdot \vec{v} - \text{div} \vec{j}_u \qquad (2)$$

is valid.

Analogously, the balance equation for mass gives

$$\operatorname{div} \rho \vec{v} + \frac{\partial \rho}{\partial t} = 0 ,$$

which can also be written

$$\rho \operatorname{div} \vec{v} + \frac{d\rho}{dt} = 0 . \tag{3}$$

The equation of motion (i.e. the momentum balance) reads

$$\rho \frac{d\vec{v}}{dt} = -\mathcal{D}iv \mathcal{P} + \rho \vec{F} , \tag{4}$$

where

$\mathcal{D}iv$ = divergence of a tensor.

If the result of a scalar multiplication of (4) by $\vec{v}$ is subtracted from (2) in a rewritten form of the latter so that it contains the convective derivative of $\frac{\vec{v}^2}{2} + u$,

$$\rho \frac{du}{dt} = -\operatorname{div} \vec{j}_u - p \operatorname{div} \vec{v} - (\mathcal{P} - p\mathcal{J}) : \operatorname{Grad} \vec{v} \tag{5}$$

is found, where

p = pressure

$\mathcal{J}$ = unit tensor

Grad = gradient of a vector,

or, if the symbol 'Φ' is introduced for the term $-(\mathcal{P} - p\mathcal{J}) : \operatorname{Grad} \vec{v}$,

$$\rho \frac{du}{dt} = -p \operatorname{div} \vec{v} - \operatorname{div} \vec{j}_u + \Phi . \tag{6}$$

For a pure, isotropic material we have, as is well known,

$$u = -p \frac{1}{\rho} + Ts + \mu ,$$

where

T = absolute temperature

s = entropy per unit mass

μ = chemical potential when the mass unit is taken as the basis instead of, as in chemistry, the number of moles.

Accordingly we have

$$\frac{du}{dt} = -p \frac{d\frac{1}{\rho}}{dt} + T \frac{ds}{dt} - \frac{1}{\rho} \frac{dp}{dt} + s \frac{dT}{dt} + \frac{dw}{dt} .$$

Since, as a consequence of the Gibbs-Duhem relation [a], the three last terms cancel out, we have for the convective derivative of u:

$$\frac{du}{dt} = -p \frac{d\frac{1}{\rho}}{dt} + T \frac{ds}{dt} ,$$

which, by means of (3), can be rewritten to

$$\frac{du}{dt} = - \frac{p}{\rho} \operatorname{div} \vec{v} + T \frac{ds}{dt} .$$

Substituted in (6), this gives

$$\rho T \frac{ds}{dt} = -\operatorname{div} \vec{j}_u + \Phi . \qquad (7)$$

(7) may be said to be an entropy balance in differential form.

If s is taken to be a function of T and p, the well-known thermodynamic formulae

$$\left(\frac{\partial s}{\partial p}\right)_T = - \left(\frac{\partial \frac{1}{\rho}}{\partial T}\right)_p$$

$$\left(\frac{\partial s}{\partial T}\right)_p = \frac{1}{T} c_p = \frac{1}{T} \cdot \text{ specific heat at constant pressure}$$

can be used to rewrite (7) into

$$\rho c_p \frac{dT}{dt} - a T \frac{dp}{dt} + \operatorname{div} \vec{j}_u - \Phi = 0 , \qquad (8)$$

where

a = the volume expansivity of the liquid.

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[a] The name 'Gibbs-Duhem relation' is in the literature often reserved for cases where p and T are constant. The relation used here may then be called 'the generalized Gibbs-Duhem relation'.

For the solution of actual problems the general balance equations do not suffice. They must be supplemented by constitutive relations, through which parameters are introduced which characterize the chemical nature of the system, as e.g. c_p and α in the above. For a pure, dielectric liquid, we have a constitutive relation of the form

$$\vec{j}_u = -\lambda \operatorname{grad} T \quad . \tag{9}$$

(9) is often termed 'Fourier's law', and λ is termed 'the thermal conductivity of the substance'.

If Fourier's law (9) is inserted in (8), we find

$$\rho c_p \frac{dT}{dt} - \alpha T \frac{dp}{dt} - \lambda \nabla^2 T - \operatorname{grad} T \cdot \operatorname{grad} \lambda - \Phi = 0 ,$$

or, if the convective derivative of T is written in full,

$$\rho c_p \frac{\partial T}{\partial t} - \lambda \nabla^2 T = -\rho c_p \vec{v} \cdot \operatorname{grad} T + \operatorname{grad} T \cdot \operatorname{grad} \lambda + \alpha T \frac{dp}{dt} + \Phi . \tag{10}$$

Only if the whole of the right side of (10) can be neglected, do we have the simple "heat flow equation"

$$\lambda \nabla^2 T - \rho c_p \frac{\partial T}{\partial t} = 0 , \tag{10a}$$

which, as previously mentioned, forms the basis of the discussions in the literature on transient methods for λ measurement on liquids. The advantage of using (10a) as one's basis is obvious: it is an equation for the T field alone, and it need only be provided with the initial and boundary conditions for this field.

The presuppositions for applying (10a) to the solution of the present problem are, as follows from the above:

1) that radiative energy transport can be neglected, and

2) that the right side of (10) can be neglected.

As to 1), a comment has been made in the above, and 2) will be discussed in the next section. In this section the following should further be mentioned: later we shall need an equation for the T field in the wire of the apparatus, i. e. in an homogeneous, isotropic metal with an electric

current. (The jump condition on the boundary between wire and liquid is that the component of $\vec{j}_u$ normal to the wire is continuous). When λ_M is a property of the metal, the desired relation can of course always be written in the form

$$\lambda_M \nabla^2 T - \rho_M c_M \frac{\partial T}{\partial t} = \Delta , \qquad (11)$$

where

ρ_M = the density of the metal

c_M = the heat capacity of the metal.

λ_M can be called 'the thermal conductivity of the metal' and Δ 'the heat production per unit volume per unit time'. It would carry us too far to discuss (11) in detail here and to set up an expression for Δ. We simply assume that, for our purpose, Δ = the density of "the Joule heat" in the wire per unit time. We thus neglect thermo-electric complications.

III. Basic Investigations of the Application of the Transient Hot-Wire Method to Pure, Dielectric Liquids

In this section the transition from (10) to (10a) is subjected to a closer investigation, which primarily means that the convection problem is treated.

Let us investigate if convection may fail to appear during the measurement period as is claimed without exception in the literature on the method known by the present author.

A characteristic treatment of the convection problem is given by Straumann [9] and by Jobst [5]. The former talks about "der Anlaufvorgang für das Entstehen der freien Konvektion", the latter about "Zeit bis zum Einsetzen der freien Konvektion". Alas [1] talks about (page 15) "(die Verlängerung)*) der konvektionsfreien Messzeit". One also finds, e.g. in the paper by Gillam et al. [4a], tabular or diagrammatic statements as to how long it takes before convection sets in for different substances and temperatures in the apparatus used. Jobst gives for example for H_2O a time of about 40 seconds, a wire diameter of 30 µm, a wire length of 15 cm and 0.1 watts per metre wire being used at 300 K.

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*) Parenthesis put by the present author.

Apparently it is assumed that mechanical equilibrium, i. e. $\vec{v} = \vec{0}$, can exist at the same time as heat flows radially out from the wire. Let g = the gravitational acceleration and x, y, z be cartesian coordinates with vertical z direction. The equation of state of the liquid is written in the form $T = T(\rho, p)$.

Mechanical equilibrium now requires

$$\frac{\partial p}{\partial x} = 0$$

$$\frac{\partial p}{\partial y} = 0$$

$$\frac{\partial p}{\partial z} = -\rho g \ .$$

If the first expression is differentiated with respect to z and the third with respect to x, the left sides become identical, and we have

$$\frac{\partial \rho}{\partial x} = 0 \ .$$

Analogously,

$$\frac{\partial \rho}{\partial y} = 0$$

is derived.

Thus neither p nor ρ must vary with x and y if mechanical equilibrium shall be established. Since $T = T(\rho,p)$, the same applies to T. In other words: only in the very special case of a temperature field where the isothermal surfaces are horizontal planes, may mechanical equilibrium be possible simultaneously with temperature differences. In that case the heat flow is vertical.

It is thus seen that convection necessarily must occur when there is a radial heat flow in the cell. Having used this argument, the present author later found it in Landau's and Lifshitz' textbook [6], page 7, in a slightly different form. True, it does not say anything about the time it takes the liquid to accelerate to a disturbing velocity field in the apparatus. But it cannot be correct, however, to talk about - in the strict sense of the word - freedom for convection for 10 to 15 seconds after the commencement of measurements. A measurement period of 10 to 15 seconds is normally

used in works that are not quite modern. The question is whether the authors concerned do not actually mean, when e. g. talking about. "Zeit bis zum Einsetzen", the time that elapses until the initial laminar convection becomes turbulent.

For if some light particles, e. g., earthmoss-seeds, are placed in the liquid before the current is switched on, and a magnifying glass is used, lively convection will be noticed long before the expiry of the measurement period (about 10 seconds). This applies in any case to cells of the "classical" kind as well as to cells modified for electrolytic measurements, which are used in the work. Ethyl alcohol, e. g., was chosen for such investigations and, with a view to later electrolytic measurements, aqueous solutions of NaCl. As far as H_2O and the aqueous solutions are concerned, it was found that the earthmoss-seeds clotted and ascended in the cells. This could be counteracted completely by adding a small amount of a surface active agent.

Various power input values within the applicable range were used and experiments were carried out in cells having diameters of 6 cm and 2 cm, and with wires of a length of about 15 cm and of diameters of 30 µm and 500 µm. In all these cases lively convection was seen at room temperature after 4 to 5 seconds, whereas all authors reckon with, as indicated, convection-free measurement periods of 10 seconds, or perhaps more.

The qualitative observation of the velocity field $\vec{v}$ described here has rendered it possible to explain why the convection, though occurring, does not disturb the measurements. This explanation is put forward in a slightly idealized form in the following (some simplification is necessary to avoid making it very complicated).

In fig. 2, W is the hot wire and R retainers between which the hot wire is stretched. In the liquid are drawn two instantaneous streamlines, which by means of earthmoss-seeds can be seen to be characteristic at any moment as long as the movement is laminar, which it seems to be beyond the measurement period of about 8 seconds used by the present author. The essential thing is that it can be said, slightly idealizing, that the direction of $\vec{v}$ is vertical everywhere in the liquid between the retainers R, i. e. in the region which in the figure corresponds to that between the lines l_1 and l_2.

Let this region be called Ω. If it can be shown that the temperature gradient in Ω is radially directed, it is thus obvious that the term $\rho c_p \vec{v} \cdot \operatorname{grad} T$ in (10) disappears, $\vec{v}$ and grad T being perpendicular to

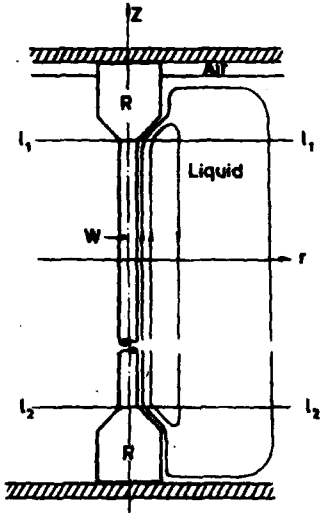

Fig. 2

each other. If the method could be called "cylinder symmetrical" in the strict sense, grad T would be radial everywhere, but as a matter of fact it is not obvious that this is so even in Ω. In the upward convection field along the wire, heat is continuously fed to the liquid, and during the measurement period the upward flow does not spread very far radially into the liquid. It is separated from the downward flow near the wall by a region in which the liquid is practically in mechanical equilibrium. According to what is said on page 15, this means that the heat flow does not reach out to this region, i. e. does not extend very far in radial direction. From this must be concluded that the temperature may very well change in vertical direction in Ω. The question is therefore whether it can be seen that $\frac{\partial T}{\partial z}$ is, if not exactly equal to 0, then approximately equal to 0, z being the vertical coordinate in a coordinate system with the z axis along the axis of the wire.

Let this coordinate system be polar, θ being the angular coordinate and r the coordinate in radial direction. When an index indicates the component of a vector in the coordinate direction concerned, we have

$$\left.\begin{aligned} v_r &= 0 \\ v_\theta &= 0 \\ \operatorname{div} \vec{v} &= \frac{\partial v_z}{\partial z} \end{aligned}\right\} \quad \text{in } \Omega \,. \tag{12}$$

According to (3), we have

$$\operatorname{div} \vec{v} = -\frac{1}{\rho}\frac{d\rho}{dt}$$

and according to the equation of state of the liquid

$$d\rho = \rho_p \, dp + \rho_T \, dT ,$$

where a subscript means partial differentiation, i.e.

$$\operatorname{div} \vec{v} = \frac{\rho_p}{\rho}\frac{dp}{dt} + \frac{\rho_T}{\rho}\frac{dT}{dt} .$$

According to Landau and Lifshitz [6], page 188, the right side of this equation can be neglected in a system like the present one, where only small differences of temperature and of pressure occur. Landau and Lifshitz emphasize that small differences of temperature are presumed, not small temperature gradients, and the condition is undoubtedly quite well fulfilled in the present case; for, as will be seen later, the wire is heated only a few degrees during the measurement period. Consequently, according to (12), we put with approximation

$$\operatorname{div} \vec{v} = \frac{\partial v_z}{\partial z} \approx 0 \qquad \text{in } \Omega . \tag{13}$$

However, in the expression for the force density in the equations of motion, the dependence of ρ on the temperature cannot be neglected*, since natural convection is due to the hot parts of the liquid becoming lighter than they are in the initial state of equilibrium, i.e. their ρ becomes smaller.

On calculating the force density, one must put

$$\rho = \rho_0 \{1 - \alpha(T-T_0)\} , \tag{14}$$

where the subscript '0' refers to the initial state in which the temperature is evenly distributed.

Using (12), (13) and (14) and the fact that the liquid is at rest at the wall of the cell because it adheres to the wall, we find as the equation of motion

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* But the dependence of ρ on the pressure can be neglected.

$$\rho_o \alpha g(T-T_o) = \rho \frac{\partial v_z}{\partial t} - \eta \left\{ \frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r} \frac{\partial v_z}{\partial r} \right\} ,$$

where

η = the viscosity of the liquid, which, on account of small T differences, is approximately constant

and

g = gravitational acceleration.

From the above it is seen that this equation has the form

$$\rho_o \alpha g(T-T_o) = \rho F(r,t) - G(r,t) , \qquad (15)$$

where 'F' and 'G' are function symbols.

If (14) and (15) are differentiated with respect to z, we find

$$\frac{\partial \rho}{\partial z} = -\rho_o \alpha \frac{\partial T}{\partial z}$$

and

$$\rho_o \alpha g \frac{\partial T}{\partial z} = F(r,t) \frac{\partial \rho}{\partial z} ,$$

from which follows

$$\rho_o \alpha \left\{ g + F(r,t) \right\} \frac{\partial T}{\partial z} = 0 .$$

With approximation we thus have

$$\frac{\partial T}{\partial z} = 0 \qquad \text{in } \Omega ,$$

which is what we wanted to demonstrate.

The temperature field is, in other words, approximately cylinder-symmetrical in Ω, i.e. $\vec{v} \cdot \text{grad } T \simeq v_z \frac{\partial T}{\partial z} \simeq 0$. The term $-\rho c_p \vec{v} \cdot \text{grad } T$ in (10) may therefore be omitted, and T is a function of only r and t in Ω.

What is said above constitutes quite another justification for neglecting the convection term in (10) in Ω than the usual one, which reads: $\vec{v} = \vec{0}$ during the measurement period, and which, according to what is said previously, is patently wrong. Applied to the present problem, (10) now reads

$$\lambda \nabla^2 T - \rho c_p \frac{\partial T}{\partial t} = -\text{grad } T \cdot \text{grad } \lambda - \alpha T \frac{dp}{dt} - \Phi .$$

It must be permissible here to neglect the first term on the right side, and this is also what Landau and Lifshitz do in treating free convection in systems with small temperature differences, loc. cit., page 212 ff.

True, it has been emphasized previously that grad T need not be numerically small, which is not the case either near the wire; but the term can be written

$$\text{grad } T \cdot \text{grad } \lambda = \frac{d\lambda}{dT} (\text{grad } T)^2$$

and $\frac{d\lambda}{dT}$ is considered, in practically all the literature on measurements, to be sufficiently small to permit the term to be neglected. If this was not permissible, (10a) would not be linear, and the mathematical and experimental difficulties would increase considerably.

As an example of λ's dependence on temperature may be mentioned that at 20 degrees centigrade, λ for ethyl alcohol decreases by about 0,15% per degree, and for water λ increases by about 0,25% per degree (up to a maximum, after which it decreases).

Now we have, in the transition to (10a), reached

$$\lambda \nabla^2 T - \rho c_p \frac{\partial T}{\partial t} = -\alpha T \frac{dp}{dt} - \Phi ,$$

and it will be in agreement with what is said previously to consider λ, ρ, c_p and α to be constant as far as the present problem is concerned. According to Landau and Lifshitz, loc. cit. page 213, it can be shown generally that the term Φ is negligible for systems with natural convection. Finally, Landau and Lifshitz omit the term $\alpha T \frac{dp}{dt}$ in the last-mentioned equation, and this, too, is in good agreement with the approximations made above. We thus have in Ω

$$\lambda \nabla^2 T - \rho c_p \frac{\partial T}{\partial t} = 0 . \qquad (10a)$$

Fig. 3 shows a cross section of the region Ω. The inner circle with radius $r = r_0$ represents the surface of the wire, and the outer circle with $r = r_c$ represents the wall of the cell. We consider a subregion of Ω bounded by two such cross sections, situated e.g. equally far below and above the middle cross section of the cell. This system is composed

of two regions: I) a piece of wire, and II) an amount of liquid.

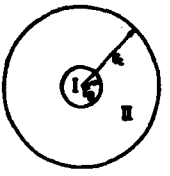

Fig. 3

We will make the simplified assumption about region I that immediately after the current is switched on at t = 0, there is a constant, i.e. an r-, z- and t-independent heat production density per time unit. This leads to a heat flow equation of the form (11) in I:

$$\lambda_W \nabla^2 T - \rho_W c_W \frac{\partial T}{\partial t} = \Delta = \text{const} \qquad \text{(A)}$$

valid in I.

Subscript 'W' indicates that the values apply to the wire material. According to what is previously said, we further have (with the accepted approximations)

$$\lambda \nabla^2 T - \rho c_p \frac{\partial T}{\partial t} = 0 \; ; \quad T \text{ cylinder-symmetrical} \qquad \text{(B)}$$

valid in II.

According to what is said on page 17 no heat will flow out to the cell wall during the measurement period, and - when it is intended to study the T field during this time interval only - the liquid can therefore be considered as infinitely extended in the r direction. When T_o is the initial temperature which is homogeneously distributed in the system, we have as initial condition

$$t = 0; \quad T = T_o, \qquad \text{(C)}$$

and as boundary condition

$$r \to \infty \; ; \quad T \to T_o \, . \qquad \text{(D)}$$

(A), (B), (C) and (D) now determine uniquely the T fields in I and II*, i.e. mathematically no further conditions can be prescribed on the bound-

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*To (A), (B), (C) and (D) must of course be added the general jump condition that the component of the heat flow density normal to a boundary surface (as between I and II) is continuous.

ing cross sections, which, e.g., would be possible if it was not known that T is cylinder-symmetrical. The mathematical proof of this assertion is of course extremely complicated. But the solution for T in both I and II is found in Carslaw and Jaeger [2], p. 347, a system being considered corresponding to the present one, but infinite in the z direction, and it is obvious that the T field under consideration here can be regarded as "cut out" of such an infinitely extended T field. Strictly speaking, a proof of uniqueness would further be required if the assertion should be supported by rigorous mathematics; however, from a physical point of view the uniqueness can hardly be questioned once a solution has been given. In [2] the solution has been written as two very complicated integral transforms. When $T_I = T$ in region I and $T_{II} = T$ in region II, they have the form

$$\left.\begin{aligned} T_I &= f(r, t, \lambda, \rho, c, \lambda_W, \rho_W, c_W) + T_o \\ T_{II} &= g(r, t, \lambda, \rho, c, \lambda_W, \rho_W, c_W) + T_o \end{aligned}\right\} \qquad (16)$$

where 'f' and 'g' are function symbols. As might have been expected, all six parameters λ, ρ, c, λ_W, ρ_W, c_W appear in both fields*. As it is an approximation to (16) which is used in connection with the treatment of the experimental data, there is no reason why the complicated formulae for T_I and T_{II} should be given here. But their application for measuring is in principle obvious: a central piece of the wire can be delimited for measurement of the resistance by means of two very thin potential leads. This limitation is imagined because the theoretical result: that T_{II} is cylinder-symmetrical, is most exactly achieved around the middle of the wire. Since an additive constant T_o does not play any part in our considerations, T_o is, for the sake of convenience, put equal to 0 here and everywhere in the following. The upper equation in (16) then reads $T_I = f(r, t, \lambda, \rho, c, \lambda_W, \rho_W, c_W)$. If the volume element of the delimited wire piece is called dv and its volume V,

$$\frac{1}{V}\int_V f\,dv = T_W$$

is the registered temperature in the wire piece. Then we have

---

* They occur in the combinations $\lambda/\rho c$ and $\lambda_W/\rho_W c_W$ = the "thermometric conductivity" of the two substances, respectively, and as λ alone.

$$T_W = F(t, \lambda, \rho, c, \lambda_W, \rho_W, c_W) \, , \tag{16a}$$

where F is a function. When all the parameters except λ are known, (16a) can be written in the form

$$T_W = \phi(t, \lambda) \, ,$$

where ϕ is registered during the experiments. If a pair of values (T_W, t) is inserted, λ can be found. (In principle several of the parameters may be found by using several pairs (T_W, t)).

The approximation to (16) used for the treatment of the experimental data referred to above is that the wire, which is of platinum, is considered to be an ideal thermal conductor, i.e. one puts $\lambda_W = \infty$, and (16a) will then have the form

$$T_W = F^*(t, \lambda, \rho, c, \rho_W, c_W) \, , \tag{16b}$$

where λ_W has disappeared, and where F^* is a new function which is simpler than F; but even the application of $T_W = F^*$ represents a rather advanced stage in the historical development of the method. In the more recent literature it is derived by assuming cylinder symmetry and $\vec{v} = \vec{0}$ beforehand and it constitutes the nowadays always accepted foundation. $T_W = F$ is not mentioned in the literature on measurements.

According to the previously quoted work by Carslaw and Jaeger (p. 344), (16b) reads

$$\left.\begin{aligned} T_W &= \frac{2q}{\pi^3 \lambda} \, a^2 \int_0^\infty \frac{1 - e^{-\frac{\varkappa t u^2}{r_0^2}}}{u^3 \, \Delta(u)} \, du \\ \text{with} \quad \Delta(u) &= \left\{ u J_0(u) - a J_1(u) \right\}^2 + \left\{ u Y_0(u) - a Y_1(u) \right\}^2 \, , \end{aligned}\right\} \tag{17}$$

where as before r_0 = radius of the wire, and

q = power per unit length of the wire

$$\varkappa = \frac{\lambda}{\rho c}$$

$$a = 2 \, \frac{\rho c}{\rho_W c_W} \, .$$

J_0, J_1, Y_0 and Y_1 are Bessel functions and they are given in appendix III

to [2]. How (17) can be used in practice to calculate λ from the quantities measured will be better understood after a discussion of the circuit of the set-up. The detailed account of this will be given in a later section.

The fact that not even the assumption leading to $T_g = F$ (which is more correct than $T_g = F^n$) is strictly correct will be dealt with briefly in the following. Neglecting thermo-electric complications, we can put Δ in (A) equal to $\vec{i}^2/\sigma_g$, where $\vec{i}$ is the electrical current density in the wire and σ_g the latter's electrical conductivity. The assumption referred to above now is that $\vec{i}^2/\sigma_g$ is independent of t and evenly distributed over the piece of wire; but immediately after t = 0, $\vec{i}$ will not be evenly distributed because induction will result in the phenomenon called "skin effect", known from the alternating current theory.

This means that, for a short while, the $\vec{i}$ field is limited to a thin "skin" around the surface of the wire; but in the present context this phenomenon can undoubtedly be considered over almost instantaneously. Then, practically speaking, $\vec{i}$ is evenly distributed, σ_g will display an r dependence over the cross sections because σ_g is T dependent, and the T profile in the r direction of the wire is not completely flat, which it would only be if the assumption $\lambda_g = \infty$ is introduced. As previously said, the temperature changes in the wire as a whole are only small, and it is therefore reasonable to neglect the variation of σ_g over the piece of the wire. However, it is not correct to neglect the dependence of σ_g (and of $\vec{i}$) on t. The very principle of the method is that the resistance of the wire changes with t so that the wire may act as a resistance thermometer. In this place, however, this is of no importance; it will later be investigated how corrections may be made for the variation of the wire power, if necessary.

The assumption $\lambda_g = \infty$ is more questionable if very precise measurements are required. The wire material is platinum, and it may be pointed out that λ_{Pt} is about one hundred times as high as e.g. $\lambda_{N_2 g}$; but strictly speaking it must be admitted that λ and λ_g do not only appear as λ/λ_g in (16a). In order to keep the work within reasonable limits, however, no further discussion about this assumption will be attempted here. Only so much should be said that experiments (to be described in a later report) seem to confirm the theoretical foundation used as a whole within the accuracy aimed at.

So far our considerations were centred on the region Ω or part of it, delimited by means of potential leads. Such a delimitation is used by several authors. It was employed already by the originators of the method, Stålhane and Pyk [10] (1931). Later Eucken and Englert [3] (1938) and Gillam et al. [4] (1955) and others used it. The cell used by Gillam et al. was sketched out in fig. 1 in section I. In that section it was also mentioned that for all who used the method it was a basic principle to operate with as thin wires as possible, e. g. 20 or 50 μm in diameter, but that this principle is departed from in this and one or more subsequent works, wires of 500 μm in diameter being used. Welding of potential leads to thin wires of a thickness like the above is very well possible; but welding is easier to perform on so robust wires as those used here, and hence the latter are very

suitable for cells with potential leads.

However, the literature also comprises works (e. g. [1] and [9]) where there are no delimitations of a central piece of the hot wire for voltage measurement, but where the full length of the wire is used, and this principle is followed here.

When the whole wire is used, fixed in retainers as indicated in fig. 2, strictly speaking certain "new boundary problems" arise; but it should not be forgotten that the use of potential leads necessitates a correction for heat transport in the leads.

The "new boundary problems" mentioned are treated in different ways in the literature; but as far as the author can see, some justified criticism can be levelled against these treatments. A very common consideration is that the thin wire is idealized to a piece of straight line source of the same length as that of the wire. This source is thought surrounded by an infinite medium at rest, with thermal conductivity equal to the λ sought for the liquid. The T field in the medium is then compared with the T field that would appear if the straight line source was infinitely long, and corrections are worked out on that basis. This method is e. g. used in [11], R. P. Tye ed., vol. 2, p. 129.

It seems to the present author that - apart from the straight line source approximation - this method does not go to the core of the problem. Undesired axial heat transport at the ends of the wire may, to some extent, be taken into account in this way. But, firstly, this transport does not take place out into the liquid but out into the wire retainers, whose properties (λ, ρ, c) are quite different from those of the liquid, and, secondly, the convection in the liquid is neglected. The liquid flows past the wire retainers and affects their temperature fields.

Furthermore, in the liquid undesired transport of heat will occur through the boundary surfaces of Ω (represented by l_1 and l_2 in fig. 2). In short: the problem is an extremely complicated jump value problem, in which the shapes and the properties of the wire and of the retainers as well as the velocity field of the liquid participate. This problem must be considered practically insoluble. Under any circumstances its solution will require sophisticated numerical methods. However, the objectionable effects of using the full wire length must in principle be reducible by shaping the wire retainers as correctly as possible and choosing the most proper material for them. The present author used stainless steel of a considerably less thermal conductivity than that of the wire (i. e. than that of platinum). The

electric conductivity of steel has also a considerably lower temperature coefficient than that of platinum. This fact and the large cross sections of the retainers permit another necessary condition to be fulfilled, viz. that it is only the wire piece between the retainers which participates in the resistance thermometer function. As an indicator of a reasonable design of wire retainers and a reasonable choice of material for the latter, one has earthmoss-seeds tests as those described. These tests are to indicate that the region where $v_r = 0$ extends in the full length of the wire, as sketched in fig. 2.

Just as important is the following: since the new boundary effects cannot be eliminated completely, calculation by means of formula (17), which presupposes cylinder symmetry, does not lead to the quite correct thermal conductivity, λ, but to a value, λ', which may be written $\lambda' = \gamma\lambda$, where γ is a function of the wire power, of the parameters of the liquid and of t for a given cell.

If one measures on a liquid with known λ and finds that λ' and λ differ p per cent, measurements on another liquid with properties similar to those of the first liquid and with the same power in the wire, will show a new p value of nearly the same magnitude for the same value of t. The new p has the same sign as the old one. When index 1 and index 2 refer to two liquids, we have

$$\frac{\lambda_1'}{\lambda_2'} = \frac{1 + \frac{p_1}{100}}{1 + \frac{p_2}{100}} \cdot \frac{\lambda_1}{\lambda_2}, \qquad (18)$$

and relative measurements may therefore reduce errors from what was called "new boundary problems" above. Measurements must then be made relative to a liquid with thermal and mechanical properties similar to those of the liquid measured on.

When, as here, the full wire length is used, it is therefore natural to measure relatively. According to this the measurements on electrolytic solutions, which will be reported later, have been relative to H_2O.

Another way in which the literature often treats the "new boundary problem" is the following: the wire is not considered a piece of straight line source, but it is assumed that the wire temperature variation in the z direction (axial) can be found from the boundary condition that $T_R = T_0$ (= 0) at the

ends (see for example: Jobst [5]), and the expression found is used for correction by a comparison with an infinitely long wire. This argument, which also only concerns the wire, may, however, be criticized on the same grounds as before. Incidentally, the practical realization of T_{Ω} = constant at the ends would require very large and very well heat-conducting wire retainers, and that would be tantamount to obtaining the most curved, instantaneous temperature profile in the z direction of the wire, whereas it is the straightest possible profile that is aimed at.

The following comments on the experiments with earthenware-seeds in the liquid should be made: looking horizontally into the cell, one will after some time see the upward moving liquid flow around the wire covered by the downward moving flow at greater distance from the wire, which is slightly puzzling. The state in the boundary zones outside Ω is also rather difficult to survey. But with some experience, the procedure must be said to be absolutely reliable. If the measurement period is exceeded materially, the actual flow will change into a form as indicated in fig. 4, where v_r clearly is not 0 near the lower part of the wire; but during the measurement period the cells used seem to give $v_r \simeq 0$ in a rather sharply defined region, Ω, corresponding to fig. 2.

Fig.4

To the method is often ascribed "an extremely reliable convection control" (Alas [1]), as certain semilogarithmic transformations of the recorder diagrams, which will be dealt with later, are said suddenly to change their direction when convection "sets in". According to what is previously said, this "change" in the diagrams transformed is caused by transition to turbulence and not by the commencement of convection.

On the general mathematical-physical foundation of the method the following comments should be made: in the literature on measurements the usual practice is not to take (17) as a starting point but the idealized solution which Eucken and Englert use in their work [3], and to set up correction terms. [3] is probably the first publication (it dates from 1938) in which it is attempted to develop the method into a precision method. Stålhane and Pyk's work [10] from 1931 - in which, as far as the present author knows, the method is worked out for the first time - appeared in a technical periodical. They used it for technical purposes, for which the highest obtainable precision was hardly required.

Eucken and Englert neglect convection in their mathematical-physical foundation and take the heat flow equation (10a) as their direct starting

point. By developing the foundation, they presuppose the heat production concentrated in the centre line of the wire, i. e. they seek the line source solution to (10a), and they presuppose the source as well as the ambient resting medium as infinite. The solution is

$$T = -\frac{q}{4\pi\lambda} \; Ei\left(-\frac{r^2}{4\varkappa t}\right), \tag{19}$$

in which Ei is the exponential integral:

$$-Ei(-x) = \int_x^\infty \frac{e^{-u}}{u}\, du,$$

and $\varkappa$ is the "thermometric conductivity" (thermal diffusivity) of the liquid:

$$\varkappa = \frac{\lambda}{\rho c} \quad .$$

q is, as previously, the power per unit length of the wire. Eucken and Englert use the approximation

$$Ei(-x) = -\ln \frac{1}{x} - 0.5772 \, ,$$

visualizing (19) used for relatively high values of t. Hence they arrive at the approximation

$$T = \frac{q}{4\pi\lambda} \left(\ln \frac{4\varkappa t}{r^2} - 0.5772\right) \tag{19a}$$

and they continue:

Measurements at two different times of the temperature at a particular point r in the field give by subtraction

$$T_2 - T_1 = \frac{q}{4\pi\lambda} \ln \frac{t_2}{t_1} \tag{19b}$$

and since r has dropped out in (19b), one may choose to measure the temperature in the cylinder axis by letting the wire work as a resistance thermometer. (19b) shows that a straight line should appear if a T versus lnt graph is drawn. If one puts

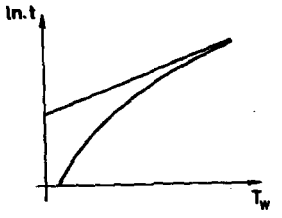
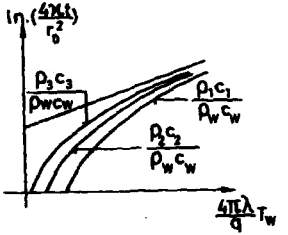


Fig. 5



Indices 1, 2 and 3 refer to different substances.

Fig. 5a

$$\frac{dT}{d\ln t} = \frac{\Delta T}{\Delta \ln t} = \psi \ ,$$

(19b) gives

$$\lambda = \frac{q}{4\pi\psi} \ . \qquad (19c)$$

The relationship between the (more) exact solution (17) for T_W and (19c) with $T = T_W$ is, as shown in the work by Carslaw and Jaeger [2], page 345, that (19c) gives the asymptote of (17) when $\pi t/r_o^2 \to \infty$. In the diagram in fig. 5, (19c) represents the straight line, whereas (17) represents the curved graph. If dimensionless coordinates are used as in fig. 5a, the solutions of (17) may be represented by a fixed family of curves, each curve corresponding to a fixed value of the parameter $\rho c / \rho_W c_W$.

All curves have the same rectilinear asymptote, represented by (19c), transformed to the new coordinates.

IV. Thermo-elastic Aspects of the Cells

In the preceding it has been mentioned that for thermo-elastic reasons a correction may occur at absolute measurements that has apparently been overlooked in the literature. In the present section this correction will be investigated. As a model of the cell the set-up shown in fig. 6 is used: a

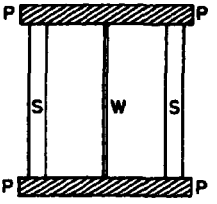


Fig.6

wire, W, stretched between two plates, P, kept apart by rods, S. This model is used because the following investigations originate in a work with a "classical" set-up* for measurement on organic reactor coolants at high temperature and pressure. The work is several years old, and rods were used then; but for the present purpose a cell such as the one of Gillam et al. might just as well be considered.

From the following sections on analysis of the circuit and calculation of λ it is now anticipated that at absolute measurements we find an expression for λ of the form

$$\lambda = F\beta \ , \qquad (20)$$

where F is a function of various magnitudes measured at λ-determinations, and β is the resistance - temperature coefficient of the wire material.

If a cell as the one shown in fig. 6 is placed in a thermostat and the wire resistance, R, is measured under equilibrium of temperature in the system at various fixed temperatures, T, a diagram can be drawn that may be called the "R versus T diagram" of the cell. The immediate impression might be that β in (20) is obtained directly by assuming the slope of the tangent $\frac{dR}{dT}$ of this diagram to be equal to βR. That is, however, wrong. Qualitatively this is due to the fact that β must = $\frac{1}{R}\frac{dR}{dT}$ in the present experiment for λ-determinations and not at recording of an R versus T diagram, and furthermore that $\frac{1}{R}\frac{dR}{dT}$ is not the same at the two operations. To prevent the rods from scattering heat back towards the wire, they are placed so far out that practically no heat reaches them during the measurement period. Consequently the rod temperature will be constant in experiments for determination of λ. At the recording of an R versus T diagram, on the other hand, the wire and S will be heated equally much at transition to a new temperature of measurement T. This difference between the two operations means that for thermo-elastic reasons $\frac{1}{R}\frac{dR}{dT}$ becomes different in the two cases. It will now be demonstrated that the difference may not be negligible.

This will necessitate the use of a formula deduced in the following small

*I. e. a set-up with a "thin" wire, 30 μm in diameter.

print.

Let us consider a wire with length l, circular cross section A, cross-sectional radius r, and resistance R at temperature T. The wire is not subjected to stress. At all temperatures one generally puts

$$R = \rho \frac{l}{A} , \tag{21}$$

and ρ is termed 'resistivity at T^0'. At a given T, ρ is a property of the material, and the same applies to

$$\beta = \frac{1}{R} \frac{dR}{dT} .$$

If, besides to varying temperature, the wire is subjected to varying tensile stress σ, l and A become functions of both σ and T:

$$l = l(\sigma,T) ; \quad A = A(\sigma,T) ,$$

and for this reason alone - i.e. because of changes in configuration of the wire - R becomes according to (21) also a function of σ as well as of T.

Experience with displacement measurements in which so-called strain gauges are used shows, however, that also ρ becomes a function of both σ and T. When a subscript means partial differentiation, we thus have

$$\left.\begin{aligned} d\rho &= \rho_\sigma \, d\sigma + \rho_T \, dT \\ dl &= l_\sigma \, d\sigma + l_T \, dT \\ dr &= r_\sigma \, d\sigma + r_T \, dT . \end{aligned}\right\} \tag{22}$$

From (21) is found

$$\frac{dR}{R} = \frac{d\rho}{\rho} + \frac{dl}{l} - \frac{dA}{A}$$

or, as $A = \pi r^2$,

$$\frac{dR}{R} = \frac{d\rho}{\rho} + \frac{dl}{l} - 2\frac{dr}{r} . \tag{23}$$

When asterisks are taken to mean the respective divisions, we furthermore find from (22)

$$\left.\begin{aligned} \frac{d\rho}{\rho} &= \rho_\sigma^* \, d\sigma + \rho_T^* \, dT \\ \frac{dl}{l} &= l_\sigma^* \, d\sigma + l_T^* \, dT \\ \frac{dr}{r} &= r_\sigma^* \, d\sigma + r_T^* \, dT \end{aligned}\right\} \qquad (22a)$$

which combined with (23) gives

$$\frac{dR}{R} = (\rho_\sigma^* + l_\sigma^* - 2r_\sigma^*)\, d\sigma + (\rho_T^* + l_T^* - 2r_T^*)\, dT . \qquad (24)$$

If this expression is used in the special case when a wire is isothermally ($dT = 0$) subjected to varying tensile stress, it is seen that

$$\frac{dR}{R} = (\rho_\sigma^* + l_\sigma^* - 2r_\sigma^*)\, d\sigma . \qquad (24a)$$

In this formula we have to a good approximation $l_\sigma^* = \frac{1}{E}$ and $r_\sigma^* = -\frac{\nu}{E}$, where E and ν are respectively the modulus of elasticity in tension and compression of the wire material and its Poisson ratio at the T in question. (This is not altogether exact, but quite sufficient here. For instance l_σ^* should be taken to be equal to $\frac{1}{1+\sigma}$ and not equal to $\frac{1}{E}$).

Thus we have for $dT = 0$

$$\frac{dR}{R} = \left(\frac{\rho_\sigma}{\rho} + \frac{1}{E} + 2\frac{\nu}{E} \right) d\sigma \qquad (25)$$

the meaning of the asterisks in (24a) having been used. As $dT = 0$, we may according to elementary theory of elasticity put

$$\frac{d\sigma}{E} = \frac{dl}{l} ,$$

and (25) then gives

$$\frac{dR}{R} = \left(\frac{\rho_\sigma}{\rho} + 1 + 2\nu \right) \frac{dl}{l} . \qquad (26)$$

The above-mentioned necessary formula is now (26), and according to this we may for $dT = 0$ write

$$\left.\begin{aligned} \frac{dR}{R} &= f \frac{dl}{l} \\ f &= E \frac{\rho_\sigma}{\rho} + 1 + 2\nu . \end{aligned}\right\} \qquad (26a)$$

The factor f is often called 'the gauge factor'. This gauge factor, which is the ratio of the relative change in resistance to the relative change in length at a given T, will play an essential part in the following. N. E. Kaiser and E. Koch assisted the author by measuring f for platinum, which is, as mentioned, the wire material in the apparatus. Kaiser and Koch set up an apparatus by means of which f could be measured directly as the ratio of $\frac{dR}{R}$ to $\frac{dl}{l}$ at various temperatures.

If in (26a) f is calculated for platinum with $\rho_\sigma = 0$, this amounts to assuming that the entire change in resistance in (26a) is due to changes in configuration. We then arrive at $f = 1.6$ at room temperature. However, Kaiser and Koch found for instance

$f = 5$ at $25^{\circ}C$ for platinum.

Thus it is evident that $\rho_\sigma \neq 0$, i.e. ρ is dependent upon the stress. Strictly speaking the same must be expected to be the case with f, but this dependence can be neglected for the present purpose.

Let P be an abbreviation for the coefficient of dT in (24). This relation can then be written

$$\frac{dR}{R} = \frac{f}{E}\, d\sigma + P\, dT\,. \qquad (27)$$

This expression is now used on the cell model, fig. 6. The cell is imagined standing in a container filled with the liquid whose λ is to be measured. The container is placed in a thermostat, and an experiment is set up during which an electric current is fed to the wire. The temperature of the wire rises, and consequently its stress, σ, changes. The experiment takes the same time (approx. 10 s) as a λ-determination so that no heating of the rods takes place. As everything happens under carefully fixed conditions, the changes mentioned will be determined by a single parameter, as e.g. time or the wire temperature T, and we may write $\sigma = \sigma(T)$, i.e.

$$d\sigma = \frac{d\sigma}{dT}\, dT\,,$$

which inserted in (27) gives

$$\frac{dR}{R} = \left\{ \frac{f}{E}\, \frac{d\sigma}{dT} + P \right\} dT$$

or

$$\frac{1}{R}\frac{dR}{dT} = \frac{f}{E}\frac{d\sigma}{dT} + P \,. \tag{28}$$

When T_S is the rod temperature, we have thus during the experiment had

$$\left.\begin{aligned} dT &\neq 0 \\ dT_S &= 0 \end{aligned}\right\} \tag{29}$$

and, when index 'corr' refers to (corrected) values during an experiment,

$$\beta_{corr} = \frac{f}{E}\frac{d\sigma}{dT} + P \,. \tag{28a}$$

One might think that of course (28) and (28a) are correct, but that quite irrespective of the splitting-up into two terms the total value of β_{corr} must be used, and consequently only R versus T recordings are to be made. However, as mentioned before $\frac{1}{R}\frac{dR}{dT}$ will at such a recording be $\neq \beta_{corr}$ because when T is raised at the recording, a new equilibrium of temperature must adjust itself in the cell at each T before R is measured. (29) is thus not valid for the recording of diagrams. On the contrary, we have for this recording

$$dT = dT_S \neq 0 \,. \tag{30}$$

To find the difference between the $\frac{1}{R}\frac{dR}{dT}$ at the two operations we must imagine the cell taken out of the thermostat and the container. Now T can be varied independently of the temperature T_S of the other parts of the apparatus. Thus it is no longer the fixed course $\sigma = \sigma(t)$ or $\sigma = \sigma(T)$ in the thermostat system that is considered, but more general transitions practicable in principle where the entire wire has a uniform temperature T and the other parts of the apparatus a different, common temperature T_S. Thus we have, when the cell is assembled with a certain, arbitrarily fixed initial stress in the wire,

$$\sigma = \sigma(T, T_S)$$

$$d\sigma = \frac{\partial \sigma}{\partial T}\,dT + \frac{\partial \sigma}{\partial T_S}\,dT_S$$

which combined with (30) gives

$$\frac{d\sigma}{dT} = \frac{\partial\sigma}{\partial T} + \frac{\partial\sigma}{\partial T_S} \quad \text{at recording of diagrams} \tag{31}$$

and with (29)

$$\frac{d\sigma}{dT} = \frac{\partial\sigma}{\partial T} \quad \text{at determinations of } \lambda. \tag{32}$$

From this follows by means of (28) and (28a) if at recording of diagrams $\frac{1}{R}\frac{dR}{dT}$ is called $'\beta_D'$

$$\left.\begin{aligned} \beta_D &= \frac{f}{E}\left\{\frac{\partial\sigma}{\partial T} + \frac{\partial\sigma}{\partial T_S}\right\} + P \\ \beta_{corr} &= \frac{f}{E}\frac{\partial\sigma}{\partial T} + P \end{aligned}\right\} \tag{33}$$

and consequently

$$\beta_{corr} = \beta_D - \frac{f}{E}\frac{\partial\sigma}{\partial T_S} \ . \tag{33a}$$

In formula (33) the partial derivatives are functions of T and T_S, but in both cases the values in the temperature-homogeneous initial state of the cell are used at an "infinitesimal change, dT", during the experiments. Thus the derivatives are to be calculated for $(T, T_S) = (T, T)$.

It has now been demonstrated that $\beta_{corr} \neq \beta_D$. We might then ask what is the relation between β_{corr} and the value β known from data literature for unstressed material, which is here taken to be $3.8\ 10^{-3}\ ^oC^{-1}$. Also there a difference is found, as with $d\sigma = 0$ (27) gives

$$\beta = P$$

i.e. according to (33)

$$\beta_{corr} = \beta + \frac{f}{E}\frac{\partial\sigma}{\partial T} \ . \tag{33b}$$

(33b) is only strictly correct if P's stress dependence is neglected. If at the assembly of the cell the initial stress of the wire is not too large, this is permissible (i.e. setting $\beta = P(0, T) \simeq P(\sigma', T)$, where σ' = the initial stress).

The correction term in (33a) may now be calculated in the following way: $\partial\sigma/\partial T_S$ is the increase in stress in the wire when the temperature

of the rods is increased by 1°, while the temperature of the wire is kept constant. If the cross-sectional area of the rods is large compared with that of the wire, the stresses in the rods may be neglected during this operation. The relative expansion of the rods then simply equals the value of the linear thermal expansivity of the rod material in its unstressed state, α_S, because the temperature is raised by 1°. If the plates are sufficiently stiff so that they do not bend, the relative expansion of the wire will equal that of the rods. As the wire temperature is kept constant, this results in the wire stress $\sigma = E_W \frac{dl}{l} = E_W \alpha_S$, where E_W (= E) is the elasticity coefficient of the wire material.

Thus

$$\frac{\partial \sigma}{\partial T_S} = E_W \alpha_S ,$$

and (33a) then takes the form

$$\beta_{corr} = \beta_D - f \alpha_S . \qquad (34a)$$

Analogously we find: constant length of the rods results in

$$\frac{dl_W}{l_W} = \frac{d\sigma}{E_W} + \alpha_W dT = 0,$$

i.e. $\frac{\partial \sigma}{\partial T} = -\alpha_W E_W = -\alpha_W E$, and (33b) then has the form

$$\beta_{corr} = \beta - f \alpha_W . \qquad (34b)$$

An example of the order of magnitude of the correction is the following: in the "classical" apparatus with which work has earlier been done with non-electrolytes, the rods were made of silver, i.e. $\alpha_S \simeq 2 \times 10^{-5}\ ^{\circ}C^{-1}$ at $20^{\circ}C$. For Pt we have, as mentioned before, $\beta \simeq 3.8 \times 10^{-3}\ ^{\circ}C^{-1}$, which will of course also be the order of magnitude for β_D. (34a) then gives for the correction in per cent

$$10^2 \frac{\beta_D - \beta_{corr}}{\beta_D} \simeq 10^2 \frac{5 \times 2 \times 10^{-5}}{3.8 \times 10^{-3}} \simeq 2.6$$

where Kaiser and Koch's value $f = 5$ is used. As $\alpha_{Pt} \simeq 9 \times 10^{-6}\ ^{\circ}C^{-1}$, (34b) gives

$$10^2 \frac{\beta - \beta_{corr}}{\beta} \simeq 1.2 .$$

If β_D or β are used without corrections at absolute measurement the result will be a corresponding error in per cent for λ, which is proportional to β_{corr}. (In (20), β means β_{corr}.)

Actually, this error did not occur in the "classical" apparatus because a helical spring had been inserted on which the upper wire retainer rested as shown in fig. 6a. But it is remarkable that the model in fig. 6 corresponds to the cell which Gillam et al. use in [4] for absolute measurements and which is sketched in fig. 1. They melt the Pt-wire slightly stretched directly into the glass cell. As far as the author understands it Gillam et al.'s text must be taken to mean that they determine what has been called 'β_D' above, and that they use it without correction. According to the above, this may result in an error of perhaps 1%, depending upon the kind of glass used for the cell. It would have been desirable if Gillam et al. had elucidated these circumstances because Gillam et al.'s work is one of the standard works often referred to owing to the careful analysis of other sources of error and to a high accuracy ($\pm$ 0.3%).

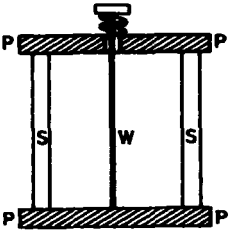


Fig.6a

The formulae developed for β_{corr} show that β_{corr} is a property of the apparatus, and that thus - in agreement with what was said in section I, page 8 - it is cancelled out at relative measurements (cf. (20)).

The above calculations are rather idealized. For instance it is presupposed that the plates do not bend. A number of experiments with the "classical" set-up were therefore made at room temperature with and without a spring for experimental verification of the assertions advanced that $\beta_{corr} \neq \beta_D \neq \beta$. As the differences are small, it was necessary to treat the material statistically.

G. Mannow kindly helped the author with this treatment, and he concluded that the experiments confirm the theory developed as far as signs

and approximate values for β_{corr} and β_D are concerned.

V. Elementary Analysis of the Electric Circuit

This section presents an elementary analysis of two circuits that have been used. One belongs to a "classical" set-up with a "thin" wire for measuring on organic reactor coolants with which work has earlier been done, cf. the preceding section, page 30. That circuit is mentioned as a basis for comparison with the other circuit that belongs to the modified set-up with a "thick" wire meant for measuring on electrolytes, cf. section I, page 9. The set-up for electrolyte measurements must in principle also be applicable for measuring on electrically non-conducting liquids, and this report only treats non-electrolytes. 'Elementary analysis' among other things is thought to mean that all complications arising from electrolytes are ignored. Further inductance, capacitance, and thermoelectric potentials in the circuit are disregarded. The analysis can then be performed solely on the basis of Kirchoff's law of nodes and Ohm's law. The cell is considered as an ohmic resistance R_C = that of the wire. The common diagram for the two set-ups is shown in fig. 7. As potential leads were not used for delimiting a length round the middle of the wire, it was possible to use a very simple circuit. As will be seen, the cell with the resistance R_C is in a Wheatstone bridge with a variable resistance R_2 and two fixed resistances

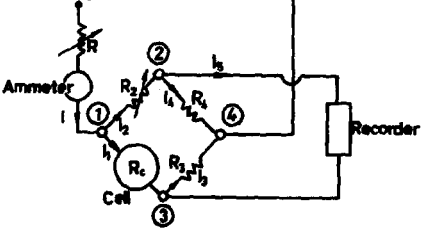


Fig.7

R_3 and R_4. Current is fed through it from a storage battery E (≈ 12 volts) through a variable resistance R, and an ammeter is inserted, which at full deflection gives an error in reading of approx. 1 o/oo of the current j running through the bridge.

With a suitably large value of R and with a reflecting galvanometer inserted in the diagonal 23, the bridge may be balanced with such a low current that the wire does not become heated during the calibration. When a recorder is then inserted in the diagonal instead of the galvanometer, and when R is changed so that j has a suitable value for the measurement, heating of the wire will change the resistance, and the unbalance thus created will be registered on the recorder as a function of time.

In the next section it will be derived how the recorder diagram and the current j read on the ammeter can be used to calculate the thermal conductivity λ of the liquid in the cell. That derivation, however, has as a necessary prerequisite the circuit analysis in this section. The two bridge set-ups are shown in fig. 8. I is the "classical" set-up, and II is the set-up

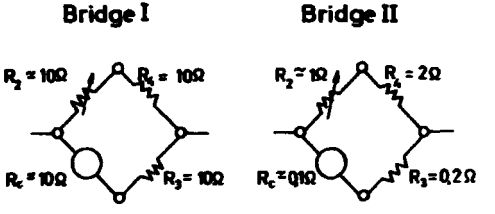


Fig.8

modified for measuring on electrolytes. Let $\Delta_{ik}\varphi = \varphi_i - \varphi_k$, where φ is voltage, and let i, k = 1, 2, 3, 4 refer to the points of fig. 7. If R_C^o is the initial value of the cell resistance R_C, we put

$$R_C = R_C^o + \Delta R_C \ .$$

When the bridge is balanced at the beginning of the experiment, we have

$$R_C^o R_4 - R_3 R_2 = 0 \ . \qquad (35)$$

If there is unbalance at the beginning of the experiment, which point arises later, we put

$$R_C^o R_4 - R_3 R_2 = d \,. \tag{36}$$

Kirchoff's law of nodes gives (see fig. 7)

$$\begin{aligned} j &= j_1 + j_2 \\ j_2 &= j_4 + j_5 \\ j_3 &= j_1 + j_5 \,. \end{aligned} \tag{37}$$

Further Ohm's law gives

$$\Delta_{12}\varphi = R_2 j_2 \qquad \Delta_{24}\varphi = R_4 j_4$$

$$\Delta_{23}\varphi = R_5 j_5 \qquad \Delta_{43}\varphi = -R_3 j_3$$

$$\Delta_{31}\varphi = -(R_C^o + \Delta R_C) j_1 \qquad \Delta_{32}\varphi = -R_5 j_5$$

$$0 = R_2 j_2 + R_5 j_5 - (R_C^o + \Delta R_C) j_1 \,. \tag{38}$$

$$0 = R_4 j_4 - R_3 j_3 - R_5 j_5 \,. \tag{39}$$

From (37), (38), and (39) we find

$$j_5 = \frac{R_C R_4 - R_3 R_2}{R_C(R_5 + R_4 + R_3) + R_5(R_2 + R_3 + R_4) + R_2 R_4 + R_3 R_2} \,,$$

from which the voltage $\Delta_{23}\varphi$ over the recorder can be calculated:

$$\Delta_{23}\varphi = j_5 R_5 = j \, \frac{R_C R_4 - R_3 R_2}{R_C\left(1 + \frac{R_4}{R_5} + \frac{R_3}{R_5}\right) + R_2 + R_3 + R_4 + \frac{R_2}{R_5} R_4 + \frac{R_3}{R_5} R_2} \,. \tag{40}$$

R_5 is of the order of magnitude $10^5 - 10^6$ Ω. In bridge No. I R_2, R_3, and R_4 are all about 10 Ω, and it is thus seen that all terms in (40) containing R_5 are negligible. This is even more pronounced in the case of bridge No. II, where R_2, R_3, and R_4 are smaller. For both bridges we thus have with a good approximation

$$\Delta_{23}\varphi = j\,\frac{R_C R_4 - R_3 R_2}{R_C + R_2 + R_3 + R_4}\ .$$

Especially for bridge No. II the approximation is extremely good. If (36) is used and the shorter designations

$$\varphi = \Delta_{23}\,\varphi \qquad (41)$$

$$\Sigma = R_C^o + R_2 + R_3 + R_4$$

are introduced, this may be written

$$\varphi = j\,\frac{R_4 \Delta R_C + d}{\Sigma + \Delta R_C}\ . \qquad (42)$$

As inductance and capacitance have been neglected, j must increase instantaneously to an initial value, j_o, when the current is switched on at t = 0.

As j varies with ΔR_C and with the terminal voltage of the battery, $j \neq j_o$ for $t \neq 0$. If, however, it can be arranged that during the measurement period $j \simeq j_o$, and that ΔR_C is negligible in comparison with Σ, (42) changes into the considerably more convenient formula

$$\varphi = j_o\,\frac{R_4 \Delta R_C + d}{\Sigma} \qquad (42a)$$

or, if for φ's instantaneously obtained initial value we write φ_o:

$$\varphi - \varphi_o = j_o\,\frac{R_4 \Delta R_C}{\Sigma} \qquad (42b)$$

with $\qquad \varphi_o = j_o\,\frac{d}{\Sigma}\ .$

As it is not known beforehand whether (42a) and (42b) are usable, φ is in these formulae now designated '$\bar{\varphi}$' instead, and the error $\frac{\varphi - \bar{\varphi}}{\varphi}$ made by replacing (42) by (42a) or (42b) is sought. We find

$$\frac{\varphi - \bar{\varphi}}{\bar{\varphi}} = \frac{\Sigma}{\Sigma + \Delta R_C}\,\frac{j - j_o}{j_o}\ . \qquad (43)$$

For estimation of this error some further relations are necessary, and

they are derived as follows:

When P is the terminal voltage, we have from fig. 7

$$j = \frac{P}{R + R_B} \quad , \tag{44}$$

where R is constant during the experiment, and R_B is the total bridge resistance, i. e.

$$R_B = \frac{(R_C+R_3)(R_2+R_4)}{\Sigma + \Delta R_C} \quad . \tag{45}$$

If ln is taken on both sides of (44), and the result is differentiated, we find

$$\frac{dj}{j} = \frac{dP}{P} - \frac{dR_B}{R+R_B} \quad . \tag{46}$$

In the same way we find from (45), where R_2, R_3, and R_4 are constant during an experiment,

$$\frac{dR_B}{R_B} = \frac{R_2+R_4}{(R_C+R_3)(\Sigma+\Delta R_C)} \; dR_C \; .$$

Thus

$$\frac{dR_B}{R+R_B} = \frac{R_B}{R+R_B} \cdot \frac{R_2+R_4}{(R_C+R_3)(\Sigma+\Delta R_C)} \; dR_C .$$

(45) used once more now gives

$$\frac{dR_B}{R+R_B} = r \; dR_C \tag{47}$$

with $$r = \frac{(R_2+R_4)^2}{R(\Sigma+\Delta R_C)^2 + (\Sigma+\Delta R_C)(R_C+R_3)(R_2+R_4)}$$

and for the variation of j we have according to (46)

$$\frac{dj}{j} = \frac{dP}{P} - r \; dR_C \; . \tag{48}$$

We then have the necessary relations to estimate the error made by replacing (42) by (42a) or (42b).

In (48) we have

$$dR_C = R_C^o \beta \, dT \ , \tag{49}$$

where β is the resistance temperature coefficient of the wire and $T = T_W$ = the wire temperature.

In the preceding section it was pointed out that it may be necessary to correct β for thermoelastic reasons; but for the present estimation it is quite sufficient to use an approximate value for platinum (at room temperature) taken from the literature. We put $\beta = 3.8 \cdot 10^{-3}$ $^oC^{-1}$ and now want to estimate how much T increases during the measurement period to be then able to estimate ΔR_C. As the thermal conductivities, the measurements of which will be described in a later report, are close to that of water, it is of interest in this report to consider experiments with water which means that $\lambda = 0.6$ W/m ^oC or $= 0.001433$ cal/cm s^oC.

In the literature one may find curves as those sketched in fig. 5a, e. g. in van der Held et al. [13] and Carslaw and Jaeger [2], and from those it is seen that (19a) with $r = r_o$ and $T = T_W$ is a sufficiently good approximation for the present purpose. In a characteristic H_2O experiment with bridge No. I the radius of the wire was 20 μm, the wire length was 18.5 cm, and $j_o \simeq 0.21$ A. (19a) gives* as the result that the rise in temperature after 10 s was $\simeq 1.2^oC$. 10 s corresponds roughly to the measurement period.

In a characteristic H_2O experiment with bridge No. II the radius of the wire was 250 μm, its length 16.7 cm, and $j_o = 3.5$ A. (19a) gives $\Delta T \simeq 3.1^oC$ after 10 s.

For such small changes in T (49) may be written in integrated form as

$$\Delta R_C = R_C^o \beta \, \Delta T \tag{49a}$$

and for the mentioned experiments it is found that for set-up No. I $\Delta R_C \simeq 7.4 \cdot 10^{-2}$ Ω after the measurement period, i.e. approx. 1 o/oo of Σ, whereas after the measurement period $\Delta R_C \simeq 1.2 \cdot 10^{-3}$ Ω, i.e. hardly

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* For this purpose the later derived formula (52) for the wire power is used. In the experiments in the "classical" set-up, (19a) corresponding to an infinitely long wire was used for absolute measurements. Therefore wire lengths of 18 to 20 cm were finally chosen, corresponding to considerably higher wire resistance than in fig. 8. Wires longer than this were impractical to handle.

$\frac{1}{2}$ o/oo of Σ for set-up No. II.

Consequently it will be permissible to neglect ΔR_C in comparison with Σ for both bridges. The approximation is best for bridge No. II, and it was slightly better for the No. II bridge used in practice, the used resistance values for bridge No. II in fig. 8 being rounded values that have been used for estimations.

For both bridges we consequently find according to (43)

$$\frac{\varphi - \bar{\varphi}}{\bar{\varphi}} = \frac{j - j_o}{j_o} .$$

As will be mentioned in the later report the variation of the terminal voltage was successfully brought down to < 0.1 o/oo after the measurement period. Because ΔR_C, as shown, is small (48) may be written as

$$\frac{j - j_o}{j_o} = \frac{P - P_o}{P_o} - r_o \, \Delta R_C ,$$

where the subscript 'o' everywhere indicates initial values. Consequently we end up with

$$\frac{\varphi - \bar{\varphi}}{\bar{\varphi}} = \frac{P - P_o}{P_o} - r_o \, \Delta R_C . \qquad (50)$$

r_o is calculated from (47) with $\Delta R_C = 0$. It is seen that r_o becomes highest when R is smallest, i.e. j highest. The highest j-values used in the No. I set-up are approx. 0.3 A, and in the No. II set-up approx. 4 A (which is very amply stated). Through a number of rather lengthy calculations it can on this basis be shown that

$$\frac{j_o - j}{j_o} = \frac{\bar{\varphi} - \varphi}{\bar{\varphi}} < 5.3 \cdot 10^{-4} \text{ for both bridges.}$$

This error is so small that in both cases (42) can be replaced by (42a) or (42b). The necessary modifications that have led from the "classical" set-up, No. I, in which (42a) and (42b) have been used, to set-up No. II have thus not had any harmful effect on this important approximation.

(42b) and (49a) then give

$$\varphi - \varphi_o = j_o \frac{R_4}{\Sigma} R_C^o \beta_{corr} \cdot T , \qquad (51)$$

β being replaced by β_{corr} because, as shown earlier, β may have to be corrected for thermoelastic reasons, and T is the wire temperature = $T_W - T_W$'s *initial* value = T_W *according to the earlier** introduced convention for the temperature zero.

(51) is one of the main results of the circuit analysis. Another main result is a calculation of the wire power and its variation during the experiments. The wire power W is found as follows.

When as before φ is the diagonal voltage $\Delta_{23}\varphi$ of the bridge, it is seen from fig. 7 that

$$j_5 = \frac{\varphi}{R_5} .$$

As R_5 is of the order of magnitude 10^5 or 10^6 Ω and φ of the order a few millivolts (which can be seen from (51)), we evidently have $j_5 \simeq 0$, and

$$j_1 \simeq j_3 ,$$

i. e.

$$\frac{\Delta_{13}\varphi}{R_C} = \frac{\Delta_{14}\varphi}{R_C + R_3} .$$

Here $\Delta_{13}\varphi = \Delta\varphi_C$ = the voltage drop over the cell, and $\Delta_{14}\varphi = R_B j$. We thus find

$$\frac{\Delta\varphi_C}{R_C} = \frac{R_B}{R_C + R_3} j$$

and from this

$$W = \frac{\Delta\varphi_C^2}{R_C} = R_C \left(\frac{R_B}{R_C + R_3} \right)^2 j^2 .$$

If finally (45) is introduced, bearing in mind that ΔR_C may be neglected in comparison with Σ, we have

$$W = R_C \left(\frac{R_2 + R_4}{\Sigma} \right)^2 j^2 . \qquad (52)$$

---

* Page 22.

For the relative change in power one can form

$$\frac{dW}{W} = \frac{R_2 + R_3 + R_4 - R_C}{R_C \Sigma} \, dR_C + 2 \frac{dj}{j}$$

or, if P is desired introduced by means of (48),

$$\frac{dW}{W} = \left(\frac{R_2 + R_3 + R_4 - R_C}{R_C \Sigma} - 2r \right) dR_C + 2 \frac{dP}{P} .$$

For small changes in R_C we thus have

$$\frac{\Delta W}{W_o} \simeq \left(\frac{R_2 + R_3 + R_4 - R_C^o}{R_C^o \Sigma} - 2r_o \right) \Delta R_C + 2 \frac{\Delta P}{P_o} . \qquad (53)$$

From the given data we find for bridge No. II that for purposes of estimation of corrections - where the essential thing is not to calculate with a too small change in power - (53) can be reduced* to

$$\frac{\Delta W}{W_o} \simeq \left(\frac{1}{R_C^o} - 2r_o \right) \Delta R_C .$$

Slightly more roughly we have

$$\frac{\Delta W}{W_o} \simeq \frac{\Delta R_C}{R_C^o} \qquad (54)$$

for estimation of the order of magnitude of $\Delta W/W_o$.

For the above-mentioned H_2O experiments we therefore have for bridge No. II

$$\frac{\Delta W}{W_o} \simeq 1.2 \cdot 10^{-2} \text{ at the end of the experiment } (t = 10 \text{ s}) .$$

For bridge No. I the results are somewhat better; but, as mentioned, the No. II set-up used in practice was built a little more favourably than corresponding to the rounded values for resistances chosen in fig. 8. In practice we have for bridge No. II had

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*ΔP is negative, ΔR_C positive. Further the factor of ΔR_C is positive.

$$\frac{\Delta W}{W_o} \ < \ 10^{-2} \ .$$

As

$$q = \frac{W}{l} \ ,$$

where l is the length of the wire, we have

$$\frac{\Delta q}{q_o} = \frac{\Delta W}{W_o} - \frac{\Delta l}{l_o} \ ,$$

where the last term is due to thermo-elastic changes that can be considered negligible. For bridge No. II we therefore have

$$\frac{\Delta q}{q_o} \simeq \frac{\Delta W}{W_o} \simeq \frac{\Delta R_C}{R_C^o} \ < \ 10^{-2} \ . \tag{55}$$

VI. Determination of the Thermal Conductivity λ from the Quantities Measured

To see how λ can be found in experiments with a set-up as outlined in fig. 7, we may, for the sake of simplicity, imagine that the bridge is in exact balance at t = 0. Then $\varphi_o = 0$ in (51). If we put

$$j_o \frac{R_4}{\Sigma} R_C^o \beta_{corr} = \alpha \ , \tag{56}$$

(51) may be written

$$\varphi = \alpha T \ \ (= \alpha T_W) \ . \tag{57}$$

The curved line in fig. 5 will, if the ordinate axis is transformed from logarithmic to ordinary t-scale and the abscissa from T to $\varphi = \alpha T$, change into a curve $K_{theor.}$ - the theoretical curve -. If this curve is drawn to a suitable scale, it will lie very close to the recorder diagram, i.e. to the recorded curve $K_{rec.}$, but as certain corrections of $K_{rec.}$ (in principle at any rate) are necessary, it cannot coincide completely with $K_{rec.}$. In

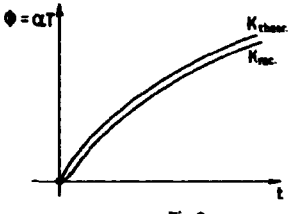

Fig.9

fig. 9* the abscissa and the ordinate are interchanged (cf. fig. 5) as this corresponds better to the experimental set-up, where a recorder with fixed paper and a recording pen moving from the left to the right was used. According to the text of fig. 5 $K_{theor.}$ corresponds to the validity of (17). As (17) presupposes that 1) q is constant and 2) that the solution is strictly cylinder symmetrical as it would be if the wire was infinitely long, the recorder diagram may as mentioned have to be corrected to give $K_{theor.}$ with a suitable accuracy. Furthermore, the recorder has a certain inertia. This is a circumstance of a more practical kind and may also give rise to a correction.

The consequences of these corrections must now be examined so that $K_{theor.}$ can be obtained from the diagram. If the corrections are sufficiently small, they can be treated independently of each other. We shall assume that this is the case. This assumption will be confirmed later.

1) Correction Owing to q's Variation

(17) is written in the form

$$T_W = T = q\,\Phi(t), \tag{58}$$

where it will be seen that Φ is a rather complicated function, and, according to the presumptions of (17), q is constant for $t > 0$. The question is now how to find the expression for T on the basis of (58), when q varies for $t > 0$.

---

* As $\frac{d^2T}{d\ln t^2} = t^2\frac{d^2T}{dt^2} + t\frac{dT}{dt}$, figs. 9 and 5 may quite well agree with each other. From fig. 9 it is seen that $\frac{dT}{dt} > 0$ and $\frac{d^2T}{dt^2} < 0$; but as $\frac{d^2T}{dt^2}$ is small and decreases greatly as t increases, $t\frac{dT}{dt}$ may become dominating on the right-hand side, i.e. $\frac{d^2T}{dt^2}$ may be < 0 even though $\frac{d^2T}{d\ln t^2} > 0$.

If the application of q does not take place at t = 0, but at t = t', it is evident that

$$T(t) = q\ \Phi(t-t')$$

when q = const. for $t > t'$.

If the application is further delayed by dt', we get

$$T(t) = q\ \Phi(t-t'-dt') = q \left\{ \Phi(t-t') - \dot{\Phi}(t-t')\ dt' \right\} ,$$

where

$$\dot{\Phi}(x) = \frac{d\Phi(x)}{dx} .$$

The difference in T(t) arising from q being applied at t'+dt' instead of at t' is thus

$$dT = -q\ \dot{\Phi}(t-t')\ dt' .$$

An alternative way of expressing this is that acting through dt', $q = q(t')$ contributes to T with

$$dT = q(t')\ \dot{\Phi}(t-t')\ dt' .$$

As the heat flow equation is linear, T may, when q varies in the time interval from 0 to t, be regarded as superposition of such infinitesimal contributions from q(t') acting through times dt'. If $q = q(t)$, we therefore find

$$T(t) = \int_0^t q(t')\ \dot{\Phi}(t-t')\ dt' . \qquad (59)$$

(59) shows how, if q varies with t, T can be found from the expression (58) for T at constant q: Φ is differentiated with respect to t, the argument is replaced by t-t'; the result is multiplied by q(t'), and an integration is made with respect to t' from 0 to t. This result may be said to be an application of the Duhamel principle. Gillon et al. [4], who are probably the first investigators trying to correct for q's variation when using the resistance thermometer method, directly - i.e. without derivation - use "Duhamel's integral" in the form

$$T(t) \frac{\partial}{\partial t} \int_0^t q(t')\ \Phi(t-t')\ dt' ,$$

in which the designations of the present work have been used*. This expression becomes identic with (59) because $\Phi(0) = 0$ on account of the convention introduced for the temperature zero, page 22. As

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* It is not clear why Gillon et al. use the operator $\frac{\partial}{\partial t}$ instead of $\frac{d}{dt}$.

(59) corresponds to $q = q_0 = \text{const.}$, (58) may, just because $\Phi(0) = 0$, be written

$$T(t) - T^* = \int_0^t q_0 \dot{\Phi}(t-t')\, dt',$$

the asterisk implying that this is the ideal solution corresponding to q = const. If we put

$$q = q_0 + \Delta q\ ,$$

the following expression is found for the error $T^* - T$:

$$T - T^* = \int_0^t \Delta q(t')\, \dot{\Phi}(t-t')\, dt'\ . \qquad (60)$$

According to the above, the question about correction owing to q-variation has in principle been solved through (60) where, as mentioned, T^* corresponds to constant q. As the correction is small, the approximate relation (54)

$$\frac{\Delta q}{q_0} = \frac{\Delta w}{w_0} = \frac{\Delta R_c}{R_c^0} = \beta_{corr}\, T \simeq \beta T$$

of the circuit analysis can be used and according to (60) we then have

$$T - T^* = \beta q_0 \int_0^t T(t')\, \dot{\Phi}(t-t')\, dt'$$

which, when Φ and T^* are known, is an integral equation for determination of T and thus of $T^* - T$. As α in (57) is constant, the change of the φ-curve into a "φ^*-curve" is also determined by that equation:

$$\varphi - \varphi^* = \alpha(T - T^*)$$

or relatively:

$$\frac{T - T^*}{T^*} = \frac{\varphi - \varphi^*}{\varphi^*}\ .$$

It is true that the λ value sought is a constituent of the expression for Φ and thus also of the mentioned integral equation, but as will be seen later, we imagine the λ-determination made iteratively, beginning with an approximately determined λ-value. The fact that 'λ' is a constituent part of

'Φ' will consequently play no part even in the case of absolute measurements where the correction for q-variation becomes necessary. As will be seen later, the correction may be neglected at relative measurements.

Further an essential remark should be made about the correction treated here, namely that it has been presupposed that the integral equation can be solved. This will not be easy as Φ and consequently $\dot{\Phi}$ are complicated functions. Therefore it is fortunate that the correction can be neglected for the present purpose. If we form

$$\frac{T-T^*}{T^*} = \frac{\int_0^t \Delta q(t') \dot{\Phi}(t-t')\, dt'}{\int_0^t q_0 \dot{\Phi}(t-t')\, dt'} ,$$

we can immediately read an upper limit for the error. Φ is namely monotone non-decreasing (follows from (17) or can be seen on curves from the literature as outlined in fig. 5a). Φ is thus $\rangle$ 0, and according to (55) this also applies to $\dot{\Phi}$. If therefore $\overline{\Delta q} = \Delta q$ at the end of the measurement period, we still have $\Delta q < \overline{\Delta q}$ and thus

$$\frac{\varphi-\varphi^*}{\varphi^*} = \frac{T-T^*}{T^*} < \frac{\overline{\Delta q} \int_0^t \dot{\Phi}(t-t')\, dt'}{q_0 \int_0^t \dot{\Phi}(t-t')\, dt'} = \frac{\overline{\Delta q}}{q_0} < 10^{-2} .$$

As $\frac{\overline{\Delta q}}{q_0}$ is small, it can be seen that, for reasons corresponding to those stated below for correction 2), correction 1) may be omitted at relative measurements. This will be elucidated in more detail in a later report dealing with measurements made (on electrolytic solutions).

As far as Gillam et al.'s measurements - which are absolute - are concerned, they use an approximation valid for large t-values for solution of the integral equation.

2) Correction Owing to the Finite Length of the Wire

In section III it was briefly mentioned that this correction may be neglected at relative measurements. This point must of course be elaborated upon, but this is best done in connection with the reporting of the experi-

ments in a later report. The chosen practical design of the apparatus with full wire length, i.e. without potential wires delimiting a section round the middle of the wire, will only result in essential errors at relative measurements without correction for finite wire length, if the 2 liquids whose λ ratio is measured have essentially different mechanical and thermal properties (cf. the remarks in section III in connection with (18)). That this is not the case at the measurements on electrolytic solutions described in a later report may be ensured for instance by measurements relative to H_2O and by restricting the measurements to diluted solutions. If the apparatus is used for other purposes, it would strictly speaking be necessary to introduce potential leads and a new circuit.

At this point, the design of the apparatus - with a view to later measurements on electrolytic solutions - may be considered as a "limiting design" usable for measurements on diluted electrolytic solutions. An analogous consideration applies to measurements on pure, dielectric liquids, and the correction problem may then be ignored.

3) Correction Owing to the Inertia of the Recorder

The recorder has 2 independent feedback systems, one for the φ-direction and one for the t-direction. In an estimate of the magnitude of the correction these systems may be symbolized by means of block diagrams as in fig. 10 corresponding to integral control with 1 time constant = τ = the time constant of the motor. Let s be the argument in Laplace trans-

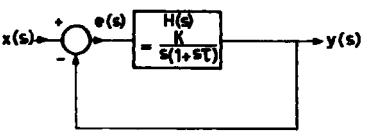

Fig.10

forms L of t. Thus we write $L[f(t)] = F(s)$ when F is f's Laplace transform, x(s) and y(s) are Laplace transforms of input and output respectively. If first the system for the φ-direction is considered, x(s) thus equals $L[\varphi_{theor.}(t)]$, where $\varphi_{theor.}$ in its turn is the ordinates of $K_{theor.}$, and

$y(s)$ is the Laplace transform of the actually recorded voltages: $y(s) = L[\varphi_{rec.}(t)]$. The permissible amplification is called K. When Δ is the error on φ, and $L[\Delta(t)] = e(s)$, we have according to the theory of feedback control

$$\left.\begin{aligned} x(s) - y(s) = e(s) &= \frac{1}{1+H(s)}\, x(s) \\ H(s) &= \frac{K}{s(1+s\tau)} \,. \end{aligned}\right\} \tag{61}$$

The error is thus obtained by transforming back the upper equation of (61).

It will be very complicated to use the actual expression (17) to find e(s). However, the recorder diagrams from the experiments resemble very much exponential curves $\varphi = \text{const.}\ (1 - e^{-at})$ with time constants

$$\frac{1}{a} \text{ between approx. 1 and 5 s.} \tag{62}$$

The value of Δ may therefore equally well be estimated by considering such curves for which it is well known that

$$x(s) = \text{const.}\ \left(\frac{1}{s} - \frac{1}{s+a}\right) .$$

Nothing is lost in generality by putting the constant equal to 1. We therefore put

$$x(s) = \frac{a}{s^2+as} ,$$

and (61) then gives

$$e(s) = \frac{1}{1 + \frac{K}{s(1+s\tau)}} \cdot \frac{a}{s^2+as} .$$

According to the theory of feedback control we may put

$$K = \frac{1}{\tau} ,$$

and we then have

$$e(s) = a\tau\, \frac{1+s\tau}{s+a} \cdot \frac{1}{s^2\tau^2+s\tau+1} . \tag{63}$$

For the recorder type used $\tau \simeq 20 \cdot 10^{-3}$ s, and if, in accordance with (62), a is chosen equal to $\frac{1}{2}\ s^{-1}$, we find by insertion in (63) and use of the operation L^{-1} on both sides approximately

$$\Delta(t) = 10^{-2} \left\{ e^{-t/2} - \frac{d}{dt} \left(\frac{1}{25\sqrt{3}}\ e^{-25t} \sin(25\sqrt{3}\ t) \right) \right\} .$$

As $e^{-t/2} \gg e^{-25t}$, when t is only somewhat greater than $\frac{1}{50}$ s, and as sin and cos is between -1 and 1, it will be seen that we shall very quickly have

$$\Delta(t) = 10^{-2}\ e^{-t/2} .$$

Thus the error Δ has been found. As it was assumed that $K_{theor.}$ has the equation $\varphi = 1 - e^{-t/2}$, the horizontal displacement $|\vec{\xi}|$ - see fig. 11 - is easily verified to be $= \tau = 2 \cdot 10^{-2}$ s for all t. $K_{rec.}$ would thus appear from $K_{theor.}$ by a parallel displacement of $2 \cdot 10^{-2}$ s if the recording pen did not also have a movement in the t-direction. This movement is controlled by feedback system No. 2, and its input is a constantly increasing voltage $= \mu t$, which is generated by the recorder. As $L[\mu t] = \frac{\mu}{s}$, the output is now found by putting $x(s) = \frac{\mu}{s}$ in (61). Calculations quite analogous to the previous ones here lead to an output curve displaced by τ seconds compared with the input curve, but this time in the opposite direction of the displacement $\vec{\xi}$ fig. 11 because the output is delayed. We thus have as the result that $\vec{\xi}$ is practically cancelled by the delay of the movement in the t-direction, and that after a very short time (slightly more than $\frac{1}{50}$ s) the recorder is free from errors. Moreover, both of the displacements $\vec{\xi}$ and $-\vec{\xi}$ are so small that it will not be possible to see them singly on account of the thickness of the line.

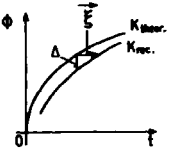

Fig. 11

In the above it was assumed that the recorder balances at t = 0, i.e. $\varphi_0 = 0$ at t = 0. The expression (42b) for φ_0 shows, however, that φ_0 is proportional to j_0 if $d \neq 0$. With the apparatus used the condition $d = 0$ cannot be fulfilled. The balancing to give $d = 0$ by means of a very small

adjusting current is always encumbered with a small error. At transition to the measurement, it is multiplied by the ratio between measuring current and adjusting current. This ratio becomes considerable. An arbitrary parallel displacement of the recorder diagrams in the φ-direction is, however, irrelevant for the following.

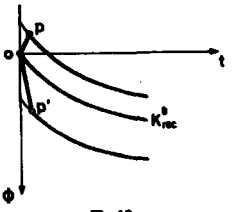

Fig. 12

In fig. 12 are shown 3 recorder curves. The φ-axis has its positive direction downwards because this corresponds best to the experimental set-up where φ was positive "downwards". $K^{o}_{rec.}$ corresponds to $\varphi_o = 0$ and will thus generally not be obtainable. The other curves are parallel displacements of $K^{o}_{rec.}$ in the φ-direction, and they correspond to 2 recordings with $\varphi_o \neq 0$ and with different signs. The displaced curves are, however, not recorded from $t = 0$ as the recording pen will reach them (with maximum velocity) a little later. Thus only the heavily drawn parts of the curves beginning with segments op or op' are observed. However, it will be possible to use the above considerations concerning errors approx. $\frac{1}{50}$ s ($= \tau$) after p or p' has been passed.

We shall now imagine an experiment with known λ, ρ, and c. According to the above the recorder may be assumed to draw $K_{theor.}$ directly. Thus we assume that $K_{theor.}$ is available for the liquid in question. Further we assume that in the literature curves as those of fig. 5a can be found with sufficiently small differences in parameter value $\rho c / \rho_W c_W$ so that transformation of the recorder diagram $K_{theor.}$ into the co-ordinates of fig. 5a results in the transformed curve coinciding with a corresponding one in the family of curves in fig. 5a. If $K_{theor.}$ for the liquid is transformed into a diagram as the one outlined in fig. 13, the result is a new, curved line with a straight-lined asymptote corresponding to the straight line in fig. 5a. At an arbitrary time t' we must, as will be seen from fig. 13, subtract a segment K from $\varphi_{theor.}$ to arrive at a corresponding point of the asymptote. As we assumed that λ, ρ, and c (and thus $a = \frac{\lambda}{\rho c}$) are known, K may be found at t' through the fig. 5a-curve

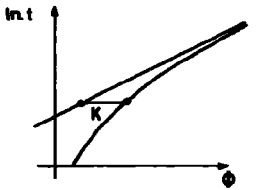

Fig. 13

for the liquid by co-ordinate transformations.

By so doing, we can evidently come from $K_{theor.}$ (the recorder diagram) to its asymptote. With a given by (56), its slope is

$$\frac{\Delta\varphi_{as}}{\Delta \ln t} = a \frac{\Delta T_{as}}{\Delta \ln t} = a\psi ,$$

where $\frac{\Delta T_{as}}{\Delta \ln t}$ has been called 'ψ', and the subscript 'as' refers to asymptote points.

According to (19c) and the remarks on page 29 we have

$$\lambda = \frac{q_o a}{4\pi\psi} . \qquad (64)$$

From (52) it is found that

$$q_o = \frac{W_o}{l} = \frac{R_c^o}{l} \left(\frac{R_2+R_4}{\Sigma}\right)^2 j_o^2 ,$$

where l = the wire length. If this is introduced into (64), and (56) is used, we have

$$\lambda = \frac{1}{4\pi} \frac{R_4 (R_c^o)^2 (R_2+R_4)^2}{l \Sigma^3 \frac{\Delta\varphi_{as}}{\Delta \ln t}} \cdot \beta_{corr} \cdot j_o^3 , \qquad (65)$$

where everything on the right-hand side will be known from the experiment. β_{corr} is mentioned in section IV, j_o is read from the ammeter, R_c^o is found by balancing of the bridge, R_2 is read directly from resistance boxes, and the other quantities, apart from $\Delta\varphi_{as}/\Delta \ln t$, are fixed in the given set-up. $\Delta\varphi_{as}/\Delta \ln t$ can be found as described in connection with fig. 13.

This experiment - where λ is known - can be used only for control of the correctness of the theoretical formula (17) and the correct functioning of the set-up. (65) may, however, also be used for λ-determination, namely when an iterative method is used. The last half or more of a part of fig. 13 corresponding to the measurement period and drawn to a suitable scale is practically straight-lined, and as a tentative value for $\Delta\varphi_{as}/\Delta \ln t$

for start of the iteration the slope of a straight line drawn as well as possible through this part of the curve can be used. ρ and c are imagined known from separate measurements or from the data literature. These 2 quantities must be known unless, as did Eucken and Englert, the line source approximation for high values of t is used (cf. (19c) page 29). This is quite inadmissible with the "thick" wires used here.

With ρ, c, and the tentative value of λ an iterative process may as mentioned be started, using the same procedure as when λ, ρ, and c are known, and in this way the segments K are increasingly better determined. The iterations may be continued until a suitable constant value for λ has been obtained.

It has been presumed here that curves as in fig. 5a can be found in the literature, and that that is the case has earlier been mentioned. In van der Held et al. [13] they are found for some values of the parameter $\rho c/\rho_W c_W$ worked out numerically. In Carslaw and Jaeger [2] page 343 they are, besides for some small parameter values as also found in van der Held et al., found for $\rho c/\rho_W c_W = \infty$.

One of the values of van der Held et al. corresponds fairly well to H_2O being the medium, only the material is too scant. Moreover, manual execution of the process becomes so time-consuming that it must be said to be impracticable at just fairly comprehensive series of measurements. The mentioned curves from the literature have, nevertheless, been a help, as will appear from the following.

At the time when the work described in this and the following report concerning measurements of λ for electrolytes had been carried out, there was at Risø no possibility of automatizing the measurement of corresponding φ- and t-values from $K_{rec.}$. Automation of this kind may, however, be carried through in a new project. Till now, $K_{rec.}$ has been measured out manually. It is true that this is rather time-consuming, but the purpose of this and the subsequent work was not to work out the fastest and most accurate method for series determinations possible. The purpose was rather to demonstrate the correctness of certain views on errors in the method and of the principle of the modification for measurement on acids, salts, and bases.

The rest of the work on the data treatment - i.e. work other than the measuring out of the curves - should, on the other hand, preferably be made on a computer, and this can also be done. N.E. Kaiser most obligingly worked out the code, and during his temporary absence the computer

section of the Reactor Physics Department at Risø assisted the author. Carslaw and Jaeger give (loc. cit. p. 345) an approximation to (17) valid for large values of the quantity $x = 4\varkappa t/r_o^2$. The formula (formula (18) in C. and J.) further includes thermal contact resistance h between wire and liquid. In the cases studied here such a resistance will only be present if the wire has been insufficiently cleaned, and as in all experiments it was degreased carefully with ether and rinsed with alcohol and water, h may be put = 0 in the above-mentioned formula. If, moreover, y is put $= \frac{4\pi\lambda T_W}{q_o}$, the formula may be written

$$y = -0.5772 + \ln x + \frac{2}{x} + \frac{2}{x}\left(1 - \frac{\rho_W c_W}{\rho c}\right)(\ln x - 0.5772) .$$

The previously mentioned curves from van der Held et al. [13] and Carslaw and Jaeger [2] were now photographically enlarged 3 times, and the axes were subdivided. This resulted in a remarkably good agreement* between the 2 sets of curves. Kaiser then introduced extra terms in the approximation formula to enlarge its range of applicability. Kaiser's formula is as follows:

$$y = -0.5772 + \ln x + \frac{2}{x} - \frac{1.5}{x^2} + \frac{2}{x}\left(1 - \frac{\rho_W c_W}{\rho c}\right)(\ln x - 0.5772)\left(1.05 - \frac{\ln x}{10}\right). \qquad (66)$$

This formula was checked by means of the mentioned enlargements of Carslaw and Jaeger's curves for some low values of the parameter $\rho c/\rho_W c_W$ and for $\rho c/\rho_W c_W = \infty$. For $\rho c/\rho_W c_W > 1$, the curves in the family of curves "up to" $\rho c/\rho_W c_W = \infty$ are so close together that this check must be considered satisfactory. Besides by the demand** $\rho c/\rho_W c_W > 1$, the range of validity of the new formula is only further limited by the condition $x \geq 5$, which simply means that the very first points of the recorder diagram should not be used. (66) was checked partly manually with single points and partly by drawing up the graph of the new formula on the computer.

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*The set of curves in [13] seems to have been worked out independently even though the authors use Carslaw and Jaeger's book.

**As will be seen in the following report, it will not be necessary to consider the case of $\rho c/\rho_W c_W < 1$ in the subsequent work.

When corresponding values of voltage and time are then read into the computer, it can perform the process described in connection with fig. 13 by means of (66). The approximation to the asymptote is determined at each step of the iteration according to the least-squares method. Practice has shown that the iteration converges, at any rate under certain further conditions to be mentioned in a later report.

In what has been written immediately above it was a presumption that the recorder registers $K_{theor.}$, or - which would be equivalent - that the recorder diagram has been corrected for errors 1), 2), and 3). Above we found that error 3), caused by the inertia of the recorder, could be ignored. Errors 1) and 2) were assumed to become negligible at relative measurements, and it is for this kind of measurements that the code has been worked out. If 2 experiments are made at the same temperature with each their liquid, and values from one experiment are denoted '1' and from the other '2' as superscripts or subscripts, and if the expression

$$\frac{\Delta\varphi_{as}}{\Delta \ln t} = \psi^*$$

is introduced, we find from (65) when furthermore index o is omitted

$$\frac{\lambda_1}{\lambda_2} = \frac{(R_2^1+R_4^1)^2}{\Sigma_1^3} \cdot \frac{\Sigma_2^3}{(R_2^2+R_4^2)^2} \cdot \frac{j_1^3}{j_2^3} \cdot \frac{\psi_2^*}{\psi_1^*} \quad . \tag{67}$$

(67) shows first that R_c, 1, and β_{corr} disappear from the calculations at relative measurement, which is a considerable help.

Secondly, (67) shows that the quantity

$$C = \frac{(R_2+R_4)^2}{\Sigma^3} \cdot \frac{j^3}{\psi^*} \cdot \frac{1}{\lambda} \tag{68}$$

is a constant determined by the apparatus when the temperature is given, i.e. C is independent of the liquid with which the experiment is made. In this author's work the measurements have been limited to room temperature (20°C).

The quantity $C^* = \lambda C$ can be determined experimentally by means of (68). Naturally, it is not determined by the apparatus, but its introduction is convenient. If C^* is determined in experiments with H_2O at 20°C, a value, $C^*_{H_2O}$, is found, and (87) shows that the thermal conductivity of a liquid relative to H_2O at 20°C can be calculated from

$$\lambda^* = \frac{\lambda}{\lambda_{H_2O}} = \frac{(R_2+R_4)^2}{\varepsilon^3} \frac{l^3}{\psi^*} \frac{1}{C^*_{H_2O}} . \qquad (69)$$

$C^*_{H_2O}$ determined experimentally is used as a fixed input value, and the computer calculates λ^* which according to what has been mentioned earlier does not need any correction of the kinds 1) and 2). Finally the computer multiplies λ^* by the most reasonable value for λ_{H_2O} at 20°C from the literature, and λ results. To this must be added that a check must be made to ensure that the corrections 1) and 2) in the H_2O-experiment have reasonably small values. If, added together, they are high, it can hardly be anticipated that the relative measurements in the work done with electrolytic solutions become correct when the corrections are omitted, unless only extremely diluted electrolytic solutions are used. However, it is easy to check that the "level" is correct with a reasonable accuracy in H_2O-experiments. C can also be calculated because the expression for λ at absolute measurement, namely (65), is known. From (65) and (68) we find

$$C = \frac{4\pi l}{R_4 R_c^2 \beta_{corr}} . \qquad (70)$$

At such a check the apparatus proved satisfactory although β_{corr} was not measured, but put = $3.8 \cdot 10^{-3}$ °C^{-1}, which may give an error of approx. 1% at the check. This check is, however, only to show that the "level" is reasonable.

Besides, a wrong "level" may be caused by many circumstances other than just boundary effects at the wire ends. Thermo-electric potentials and not-negligible supply resistances, among these contact resistances, may be present. If such supply resistances become appreciably heated during the experiments, quite uncontrollable sources of errors are introduced. The recorder must only register unbalance caused by heating of the wire between the retainers.

Control that turbulence does not disturb the measurement will be mentioned in the following report on measurements on elelctrolytic solutions.

VII. Comments on the Accuracy of Determinations of λ as well as on Other Measuring Methods of λ

L. Riedel describes in the introduction to one of his works [8] his surprise when he found - while working on the thermal conductivity of liquids at a refrigeration research institute - that as late as in 1938 it had not yet been possible to decide which measurements were the better: P.W. Bridgman's from 1922 on so ordinary liquids as benzene, toluene and acetone, or H.F. Weber's from 1887 on the same liquids. Weber's values are about 10% lower than those of Bridgman.

In a work [9] from 1960, W. Straumann says:

"Vergleicht man die nach verschiedenen Verfahren gemessene Wärmeleitfähigkeit eines bestimmten Stoffes, so erkennt man an der grossen Streuung, dass die genaue Messung der Wärmeleitfähigkeit offenbar äusserst schwierig ist."

From diagrams in Strauman's work with plotted values given by various researchers, differences are read of about 16% for ethyl alcohol at 20°C and about 9% for glycerol at 20°C.

The literature gives the reader the impression that the situation has not improved much in the period of about 20 years between Riedel's and Straumann's works, and that in fact it is unchanged. This impression is confirmed by reading the preface of the composite work published by R.P. Tye [11]. This work dating from 1969 must be considered up-to-date. From this is quoted:

"A number of examples can be quoted in which separately reported values of the thermal conductivity of a particular material may differ by an order of magnitude and many other cases where the difference is often at least ten times the claimed accuracy for the measurement technique used."

It is said loc. cit. that "confusion" prevails within the field and that critical judgement of the methods is necessary. Further, it is stated that before World War II, technology was at a stage where ± 20% was often sufficient. Nowadays - it is said - ± 10% for engineering purposes and ± 2% for basic studies are the absolutely minimal demands, and it is predicted that these claims will soon be replaced by severer ones.

The literature includes a great number of works. A rather comprehensive survey of these is given in the work by Straumann [9] (1960), in the work of Alas [2] (1967) and in the composite work [11] (1969).

Various attempts have been made to evade the difficulties. Steady state as well as transient methods are worked out and within both categories different geometrical layouts have been used.

Each author tends to claim that his category and his geometrical layout are the best. W. Leidenfrost says, e. g., in a work [7] from 1964 (p. 449): "It does not need to be discussed here that highly accurate measurements dictate an absolutely steady state method". He indicates that his "experimental accuracy" is 0. 1%. In the work by Gillam et al. from 1955 [8] on transient hot-wire measurement, the accuracy is reported to be $\pm$0. 3%, which is not much inferior to that of Leidenfrost.

As to the geometrical layout the following applies: usually the liquid is contained in a region which may be termed 'the gap' bounded by two closed surfaces, one inside the other. The heat source is almost always electrical and so shaped that the surfaces are as nearly isothermal as possible. Examples of geometrical layouts, which have all been used for apparatuses described in the literature, are given in fig. 14, showing (hatched) sections in the liquid regions. These regions are generated by rotation of the sections around the symmetry axes. The disc-shaped gap (fig. 14a) requires a heat source evenly distributed over the upper bounding plane. For the cylindrical gaps* (figures 14b and 14d) heat

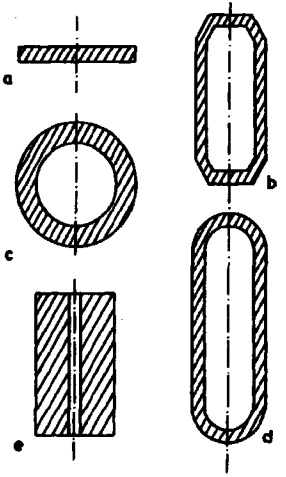

Fig. 14

* Apparatuses of this kind are usually termed 'cylinder symmetrical'.

sources, which are co-axial with the cylinders, are needed. For the spherical gap (fig. 14c) an approximation to a point source in the centre is required. Fig. 14e is a variant of a cylindrical layout with axially placed hot wire, the surface of which constitutes the inner isothermal surface. In principle all designs may be used for both steady state and transient measurements. Difficulties at the boundaries of the region of the liquid appear in one or more forms in all cases. One of these difficulties is the exact making of the boundaries themselves for the desired shape; and for some types there are also centering problems.

The type in fig. 1a requires that the heat source is absolutely uniform so that differences of temperature do not occur in the bounding planes. At the radial boundary of the liquid lamella, complications arise which are usually sought remedied by building in so-called "guard heaters". So the problem consists in making the bounding planes absolutely isothermal and in forcing the generated heat to run only vertically down through the horizontally placed liquid lamella. The difficulties in guiding the heat flow are in other types sought evaded by having the liquid totally surround the heat source, but of course this necessitates the liquid layer to be broken by leads and through these leads unwanted transport of heat can take place. The type fig. 1c probably has the shape which theoretically gives the best isothermal surfaces provided the shape is accurately made.

The investigations in section III showed that in principle natural convection must occur in all types during measurement with the exception of an ideally operating apparatus of the type shown in fig. 14a. In a few exceptional cases methods have been used based on forced convection, the intention being to control convection instead of eliminating it approximately (e.g. by very narrow gaps). In A Dictionary of Applied Physics (2nd edition, Peter Smith 1950), volume I, page 454, are thus mentioned Callendar's method, according to which the liquid flows through a heated tube, and Nettleton's method, which also builds upon forced convection.

The transient methods involve the greatest mathematical difficulties. On the other hand, certain practical advantages may attach to these methods. Their short measurement period is often emphasized. As an advantage of transient measurement it is often put forward that steady state methods require a long time for obtaining the steady state, but e.g. the transient hot-wire method also requires some time for temperature equilibrium to be obtained in the initial state. A certain "elegance" is often claimed for the last-mentioned method. However, any absolutely decisive argumentation in favour of this method's superiority to other methods is not, in the opinion of the author, adducible. It seems difficult to find objective criteria according to which one method could be claimed to be the best one in all respects.

The many methods should rather be considered supplementing and controlling each other. Mutually controlling of measurement values for the same quantity obtained by different methods is an important aspect of scientific procedure.

Quite apart from the attempts to evaluate the various methods for the determination of λ, one may claim that during the last 30 years the use of transient hot-wire measurements has become more extensive at the expense of other methods.

References

[1] Alas, Chiquillo, Messung der relativen Wärmeleitfähigkeit wässriger Salzlösungen nach einem instationären Hitzdrahtverfahren. Dissertation Eidgenössische Technische Hochschule Nr. 3955 (Juris Verlag, Zürich, 1967) 77 pp.

[2] Carslaw, H.S. and Jaeger, J.C., Conduction of Heat in Solids, 2nd edition (Clarendon Press, Oxford, 1959) 510 pp.

[3] Eucken, A. and Englert, H., Z. ges. Kälteind. 45 (1938) 109-118.

[4] Gillam, D.G., Romben, L., Nissen, H., and Lamm, O., Acta Chem. Scand. 9 (1955) 641-656.

[4a] Gillam, D.G. and Lamm, O., Acta Chem. Scand. 9 (1955) 657-660.

[5] Jobst, W., Messung der Wärmeleitfähigkeit von organischen, aliphatischen Flüssigkeiten und von Gasen nach einem instationären Absolutverfahren. Dissertation Eidgenössische Technische Hochschule Nr. 3547. (Zürich, 1964) 60 pp.

[6] Landau, L.D. and Lifshitz, E.M., Fluid Mechanics. (Pergamon Press, London, 1959) 536 pp.

[7] Leidenfrost, W., Int. J. Heat Mass Transfer 7 (1964) 447-478.

[8] Riedel, L., Wärmeleitfähigkeitsmessungen an Flüssigkeiten. (C.F. Müller Verlag, Karlsruhe, 1948) 47 pp.

[9] Straumann, W., Ein instationäres Verfahren zur Messung der Wärmeleitfähigkeit von Flüssigkeiten und Gasen. Dissertation Eidgenössische Technische Hockschule Nr. 3078. (Solothurn, Zürich, 1960) 27 pp.

[10] Stålhane, B. and Pyk, S., Tekn. Tidsskrift A61 (1931) 389-393.

[11] Tye, R.P. (editor), Thermal Conductivity. (Academic Press, London, 1969) Vol. 1-2.

[12] van der Held, E.F.M. and van Drunen, F.G., Physica 15 (1949) 865-881.

[13] van der Held, E.F.M., Hardebol, J., and Kalshoven, J., Physica 19 (1953) 208-216.

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